

EXHIBIT A

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IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

BRIDGESTONE SPORTS CO.,)
LTD.,)
)
 Plaintiff,)
) C.A. No. 05-143-JJF
v.)
)
ACUSHNET COMPANY,)
)
 Defendant.)

August 2, 2006
10:07 a.m.
Courtroom 4B

844 King Street
Wilmington, Delaware

BEFORE: THE HONORABLE JOSEPH J. FARNAN, JR.
United States District Court Judge

APPEARANCES:

MORRIS, NICHOLS, ARSHT & TUNNELL
BY: JACK B. BLUMENFELD, ESQ.

-and-

PAUL HASTINGS
BY: ROBERT M. MASTERS, ESQ.
BY: TERRENCE J. WIKBERG, ESQ.

Counsel for Plaintiff

1 original document production request, although
2 the issues haven't changed, there may be some
3 reduced expectation that is appropriate, because
4 now production will be against what it is that
5 are representative claims and defenses.

6 Anything else?

7 MR. GRIMALDI: No, Your Honor.

8 THE COURT: On behalf of
9 Bridgestone?

10 MR. MASTERS: Yes, Your Honor.

11 Earlier you referred to Acushnet having to limit
12 their invalidity contentions by limiting the
13 number of references, but you did not place a
14 number on the references or the number of
15 positions.

16 THE COURT: Well, I didn't place
17 that specifically, because this is a very crowded
18 art field apparently.

19 MR. MASTERS: It can be.

20 THE COURT: Yeah, from what I read.

21 I mean, I think you set out just what they've
22 talked about, 50 something here.

23 So let's see how reasonable they
24 want to be with you, and if it's truly supportive

EXHIBIT B



US006486261B1

(12) **United States Patent**
Wu et al.

(10) Patent No.: **US 6,486,261 B1**

(45) Date of Patent: **Nov. 26, 2002**

(54) **THIN-LAYER-COVERED GOLF BALL WITH IMPROVED VELOCITY**

(75) Inventors: Shenshen Wu, North Dartmouth, MA (US); Edmund A. Hebert, Fairhaven, MA (US); Laurent Bissonnette, Portsmouth, RI (US); David A. Bulpett, Boston, MA (US); Murali Rajagopalan, South Dartmouth, MA (US); Peter Voorheis, Fall River, MA (US); Mark N. Wrigley, New Bedford, MA (US)

(73) Assignee: Acushnet Company, Fairhaven, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 45 days.

(21) Appl. No.: 09/721,740

(22) Filed: Nov. 27, 2000

Related U.S. Application Data

(63) Continuation-in-part of application No. 09/461,736, filed on Dec. 16, 1999, and a continuation-in-part of application No. 09/311,591, filed on May 14, 1999, now Pat. No. 6,210,294, and a continuation-in-part of application No. 09/274,015, filed on Mar. 22, 1999.

(60) Provisional application No. 60/113,949, filed on Dec. 24, 1998.

(51) Int. Cl.⁷ A63B 37/12; A63B 37/06

(52) U.S. Cl. 525/332.6; 525/332.5; 525/274; 473/374; 473/376; 473/377; 473/378

(58) Field of Search 525/274, 332.6, 525/332.5; 473/374, 376, 377, 378

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,147,324 A	9/1964	Ward	264/254
3,239,228 A	3/1966	Crompton	273/218
3,572,721 A	3/1971	Harrison et al.	372/218
3,572,722 A	3/1971	Harrison et al.	273/218
3,804,421 A	4/1974	Alex et al.	273/218
3,808,077 A	4/1974	Rieser et al.	156/102
3,989,568 A	11/1976	Isaac	156/182
3,992,014 A	11/1976	Retford	273/218
4,062,825 A	12/1977	Watabe et al.	260/37 N
4,123,061 A	10/1978	Dusibier	273/220
4,274,637 A	6/1981	Molitor	273/235 R
4,310,582 A	1/1982	Stampe, Jr.	428/182

4,650,193 A	3/1987	Molitor et al.	273/228
4,692,497 A	9/1987	Gendreau et al.	525/263
4,931,376 A	6/1990	Ikematsu et al.	526/164
4,971,329 A	11/1990	Llort et al.	273/218
5,017,636 A	5/1991	Hattori et al.	524/300
5,025,059 A	6/1991	Mouri et al.	524/495
5,131,662 A	7/1992	Pollitt	273/230
5,141,233 A	8/1992	Yuki et al.	273/218
5,252,652 A	10/1993	Egashira et al.	524/392
5,421,580 A	6/1995	Sugimoto et al.	273/227
5,461,109 A	10/1995	Blair et al.	524/839
5,496,496 A	3/1996	Kajita et al.	252/182.24
5,585,440 A	12/1996	Yamada et al.	525/193
5,587,420 A	12/1996	Takizawa et al.	524/572
5,697,856 A	12/1997	Moriyama et al.	473/374
5,744,549 A	4/1998	Lutz	525/129
5,779,561 A	7/1998	Sullivan et al.	473/373
5,803,831 A	9/1998	Sullivan et al.	473/374
5,816,944 A	10/1998	Asakura et al.	473/372
5,827,134 A	10/1998	Sullivan et al.	473/372
5,856,388 A	1/1999	Harris et al.	524/320
5,859,153 A	1/1999	Kirk et al.	525/481
5,861,465 A	1/1999	Hamada et al.	525/332.6
5,885,173 A	3/1999	Keller	473/385
5,919,101 A	7/1999	Yokota et al.	473/374
5,929,171 A	7/1999	Sano et al.	525/261
6,012,997 A	1/2000	Mason	473/594
6,190,268 B1 *	2/2001	Dewanjee	
6,290,611 B1 *	9/2001	Rajagopalan	
6,309,313 B1 *	10/2001	Peter	
6,315,684 B1 *	11/2001	Binette	

FOREIGN PATENT DOCUMENTS

AU	A-16547/97	2/1997
AU	A-16548/97	2/1997
EP	0 577 058 A1	1/1994
EP	0 903 357 A1	3/1999
GB	1 168 609	10/1969
GB	1 209 032	10/1970
GB	2 321 021 A	3/1997

* cited by examiner

Primary Examiner—David J. Buttner

(74) Attorney, Agent, or Firm—Swidler Berlin Shereff Friedman, LLP

(57) **ABSTRACT**

A golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 200,000 and a resilience index of at least about 40; and a cover layer comprising a polyurethane composition formed from a pre-polymer having no greater than 7.5 percent by weight unreacted isocyanate groups.

50 Claims, 1 Drawing Sheet

U.S. Patent

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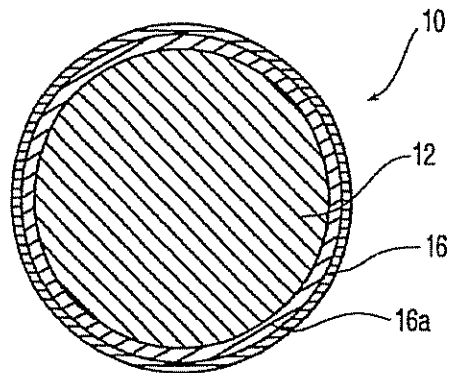


Fig. 1

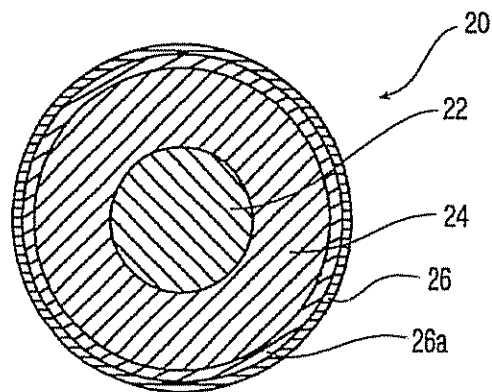


Fig. 2

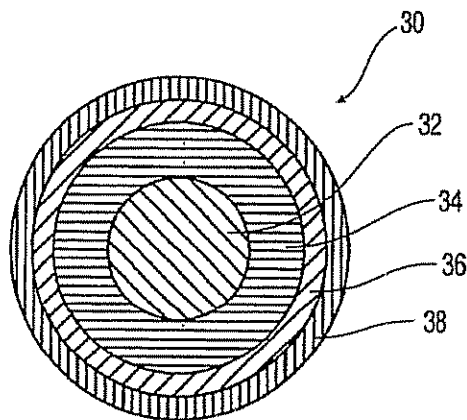


Fig. 3

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**THIN-LAYER-COVERED GOLF BALL WITH
IMPROVED VELOCITY****CROSS-REFERENCE TO RELATED
APPLICATIONS**

This application is a continuation-in-part of co-pending U.S. patent application Ser. No. 09/461,736, filed Dec. 16, 1999, which claims the benefit of provisional U.S. patent application No. 60/113,949, filed Dec. 24, 1998, a continuation-in-part of U.S. patent application Ser. No. 09/311,591, filed May 14, 1999, now U.S. Pat. No. 6,210,294 and also a continuation-in-part of co-pending U.S. patent application Ser. No. 09/274,015, filed Mar. 22, 1999.

FIELD OF THE INVENTION

The invention relates generally to golf balls, and more specifically, to golf balls with covers formed of a polymer blend comprising a polyurethane composition and cores formed of a polybutadiene composition. The polyurethane composition comprises a prepolymer of a polyisocyanate and a polyol, and a diamine curing agent. The polybutadiene composition comprises a butadiene polymer with a resilience index greater than about 40 and a molecular weight greater than about 200,000. The golf balls of the present invention have been found to provide improved velocity.

BACKGROUND OF THE INVENTION

Conventional golf balls can be divided into several general classes: (a) solid golf balls having one or more layers, and (b) wound golf balls. Solid golf balls include one-piece balls, which are easy to construct and relatively inexpensive, but have poor playing characteristics and are thus generally limited for use as range balls. Two-piece balls are constructed with a generally solid core and a cover and are generally the most popular with recreational golfers because they are very durable and provide maximum distance. Balls having a two-piece construction are commonly formed of a polymeric core encased by a cover. Typically, the core is formed from polybutadiene that is chemically crosslinked with zinc diacrylate and/or other similar crosslinking agents. These balls are generally easy to manufacture, but are regarded as having limited playing characteristics. Solid golf balls also include multi-layer golf balls that are comprised of a solid core of one or more layers and/or a cover of one or more layers. These balls are regarded as having an extended range of playing characteristics.

Wound golf balls are generally preferred by many players due to their high spin and soft "feel" characteristics. Wound golfballs typically include a solid, hollow, or fluid-filled center, surrounded by a tensioned elastomeric material and a cover. Wound balls generally are more difficult and expensive to manufacture than solid two-piece balls.

A variety of golf balls have been designed by manufacturers to provide a wide range of playing characteristics, such as compression, velocity, "feel," and spin. These characteristics can be optimized for various playing abilities. One of the most common components that manufacturers have addresses for optimizing and/or altering the playing characteristics of golf balls, is the polymer components present in modern golf ball construction, in particular, golf ball centers and/or core. In addition to ionomers, one of the most common polymers employed is polybutadiene and, more specifically, polybutadiene having a high cis-isomer concentration.

The use of a polybutadiene having a high cis-concentration results in a very resilient and rigid golf ball,

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especially when coupled with a hard cover material. These highly resilient golf balls have a relatively hard "feel" when struck by a club. Soft "feel" golf balls constructed with a high cis-polybutadiene have low resilience. In an effort to provide improved golf balls, various other polybutadiene formulations have been prepared, as discussed below.

U.S. Pat. No. 3,239,228 discloses a solid golf ball having a core molded of polybutadiene rubber with a high sulfur content, and a cover. The polybutadiene content of the core is stereo-controlled to the configuration 25–100 percent cis- and 0–65 percent trans-1,4-polybutadiene, with any remainder having a vinyl configuration of polybutadiene. A preferred embodiment of the polybutadiene golf ball core contains 35 percent cis-, 52 percent trans-, and 13 percent vinyl-polybutadiene. The level of trans- and vinyl-content are disclosed to be unimportant to the overall playing characteristics of the polymer blend.

British Patent No. 1,168,609 discloses a molding composition from which improved golf ball cores can be molded and which contains cis-polybutadiene as a basic polymer component. The core polymer component typically includes at least 60 percent cis-polybutadiene, with the remainder being either the trans- or vinyl-forms of polybutadiene. In a preferred embodiment, the core polybutadiene component contains 90 percent cis-configuration, with the remaining 10 percent being either the trans- or vinyl-configurations of 1,4-polybutadiene.

U.S. Pat. Nos. 3,572,721 and 3,572,722 disclose a solid, one- or two-piece golf ball, with the two-piece ball having a core and a cover. The cover material can include any one of a number of materials, or blends thereof, known to those of ordinary skill in the art, including trans-polybutadiene which may be present in an amount from at least 90 percent, with the remainder being the cis- and/or vinyl configuration.

British Patent No. 1,209,032 discloses a two- or three-piece golf ball having a core and a cover. The core or cover material can be any material capable of being crosslinked. In particular, the material can be a polymer or a copolymer of butadiene or isoprene. Preferably, the polymer component is polybutadiene having a cis content of greater than 50 percent by weight.

U.S. Pat. No. 3,992,014 discloses a one-piece, solid golf ball. The golf ball material is typically polybutadiene, with a stereo-configuration selected to be at least 60 percent cis-polybutadiene, with the remaining 40 percent being the trans-polybutadiene and/or 1,2-polybutadiene (vinyl) isomers.

U.S. Pat. No. 4,692,497 discloses a golf ball and material thereof formed by curing a diene polymer including polybutadiene and a metal salt of an alpha, beta ethylenically unsaturated acid using at least two free radical initiators.

U.S. Pat. No. 4,931,376 discloses a process for producing butadiene polymers for use in various applications, including golf ball cover materials. One embodiment of the invention employs a blended polymeric resin material, including at least percent by weight of a trans-polybutadiene polymer as a golf ball cover on a two-piece ball. In a preferred embodiment, the golf ball cover material contains a blend including 30 to 90 percent by weight of a trans-polybutadiene polymer.

U.S. Pat. No. 4,971,329 discloses a solid golf ball made from a polybutadiene admixture of cis-1,4 polybutadiene and 1,2 polybutadiene, a metal salt of an unsaturated carboxylic acid, an inorganic filler, and a free radical initiator. The admixture has about 99.5 percent to about 95 percent by weight of cis-1,4 polybutadiene and about 0.5 percent to about 5 percent by weight of 1,2 polybutadiene.

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U.S. Pat. No. 5,252,652 discloses a one-piece or multi-layered golf ball core with improved flying performance from a rubber composition comprising a base rubber, preferably 1,4-polybutadiene with a cis-content of at least 40 mole percent, an unsaturated carboxylic acid metal salt, an organic peroxide, and an organic sulfur compound and/or a metal salt thereof. The organic sulfur compound and/or a metal salt is typically present in an amount from about 0.05 to 2 parts per hundred by weight and the organic peroxide is typically present in an amount from about 0.5 to 3 parts per hundred by weight of the total polymer component.

European Patent No. 0 577 058 discloses a golf ball containing a core and a cover that is formed as two separate layers. The inner layer of the cover is molded over the core and is formed from ionomer resin. The outer layer of the cover is molded over the inner layer and is formed from a blend of natural or synthetic balata and a crosslinkable elastomer, such as polybutadiene. In one embodiment of the outer layer of the cover, the elastomer is 1,4-polybutadiene having a cis-structure of at least 40 percent, with the remaining 60 percent being the trans-isomer. A preferred embodiment contains a cis-structure of at least 90 percent and more preferably, a cis-structure of at least 95 percent.

U.S. Pat. No. 5,421,580 discloses a wound golf ball having a liquid center contained in a center bag, a rubber thread layer formed on the liquid center, and a cover over the wound layer and liquid center. The cover material can include any one of a number of materials, or blends thereof, known to those of ordinary skill in the art, including trans-polybutadiene and/or 1,2-polybutadiene (vinyl), such that the cover has a JIS-C hardness of 70-85; preferred trans-percentages are not disclosed.

U.S. Pat. No. 5,697,856 discloses a solid golf ball having a core and a cover wherein the core is produced by vulcanizing a base rubber composition containing a butadiene rubber having, a cis-polybutadiene structure content of not less than 90 percent before vulcanization. The amount of trans-polybutadiene structure present after vulcanization is 10 to 30 percent, as amounts over 30 percent are alleged to detrimentally result in cores that are too soft with deteriorated resilience performance, and to cause a decrease in golf ball performance. The core includes a vulcanizing agent, a filler, an organic peroxide, and an organosulfur compound.

British Patent No. 2,321,021 discloses a solid golf ball having a core and a cover formed on the core and having a two-layered cover construction having an inner cover layer and an outer cover layer. The outer cover layer is comprised of a rubber composite that contains 0.05 to 5 parts by weight of an organic sulfide compound. The core rubber composition comprises a base rubber, preferably 1,4-polybutadiene having a cis-content of at least 40 percent by weight, a crosslinking agent, a co-crosslinking agent, an organic sulfide, and a filler. The crosslinking agent is typically an organic peroxide present in an amount from 0.3 to 5.0 parts by weight and the co-crosslinking agent is typically a metal salt of an unsaturated fatty acid present in an amount from 10 to 40 parts by weight. The organic sulfide compound is typically present from 0.05 to 5 parts by weight.

U.S. Pat. No. 5,816,944 discloses a solid golf ball having a core and a cover wherein the core has a JIS-C hardness of 50 to 80 and the cover has a Shore-D hardness of 50 to 60. The core material includes vulcanized rubber, such as cis-polybutadiene, with a crosslinker, an organic peroxide, an organosulfur compound and/or a metal-containing organosulfur compound, and a filler.

Additionally, conventional polymers that have a high percentage of the trans-polybutadiene conformation, such as

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DIENE 35NF, from Firestone Corp., that has 40 percent cis-isomer and 50 percent trans-polybutadiene isomer, and mixtures of high-cis- and high-trans-polybutadiene isomers, such as CARIFLEX BR1220, from Shell Corporation, and FUREN 88, from Asahi Chemical Co., respectively, typically do not yield high resilience values and therefore are not desirable.

In addition to changing center or core ingredients to affect golf ball performance characteristics, a number of patents have issued that are directed towards modifying the properties of layers and covers used in forming a variety of golf balls, such as wound balls, conventional solid balls, multi-layer balls having dual cover layers, dual core layers, and/or balls having a mantle layer disposed between the cover and the core. The most common polymers used by manufacturers in golf ball layers and covers have been ionomers, such as SURLYN, commercially available from E.I. DuPont de Nemours and Co., of Wilmington, Del. Recently, however, manufacturers have investigated the use of alternative polymers, such as polyurethane. For example, U.S. Pat. No. 3,147,324 is directed to a method of making a golf ball having a polyurethane cover.

Polyurethanes have been recognized as useful materials for golf ball covers since about 1960. Polyurethane is the product of a reaction between a polyurethane prepolymer and a curing agent. The polyurethane prepolymer is a product formed by a reaction between a polyol and a diisocyanate. The curing agents used previously are typically diamines or glycols. A catalyst is often employed to promote the reaction between the curing agent and the polyurethane prepolymer.

Since 1960, various companies have investigated the usefulness of polyurethane as a golf ball cover material. U.S. Pat. No. 4,123,061 teaches a golf ball made from a polyurethane prepolymer of polyether and a curing agent, such as a trifunctional polyol, a tetrafunctional polyol, or a diamine. U.S. Pat. No. 5,334,673 discloses the use of two categories of polyurethane available on the market, i.e., thermoset and thermoplastic polyurethanes, for forming golf ball covers and, in particular, thermoset polyurethane covered golf balls made from a composition of polyurethane prepolymer and a slow-reacting amine curing agent, and/or a difunctional glycol. The first commercially successful polyurethane covered golf ball was the Titleist® Professional ball, first released in 1993.

Unlike SURLYN® or ionomer-covered golf balls, polyurethane golf ball covers can be formulated to possess the soft "feel" of balata covered golf balls. However, golf ball covers made from polyurethane have not, to date, fully matched SURLYN®-covered golf balls with respect to resilience or the rebound that is a function of the initial velocity of a golf ball after impact with a golf club.

U.S. Pat. No. 3,989,568 discloses a three-component system employing either one or two polyurethane prepolymers and one or two polyols or fast-reacting diamine curing agents. The reactants chosen for the system must have different rates of reactions within two or more competing reactions.

U.S. Pat. No. 4,123,061 discloses a golf ball made from a polyurethane prepolymer of polyether and a curing agent, such as a trifunctional polyol, a tetrafunctional polyol, or a fast-reacting diamine curing agent.

U.S. Pat. No. 5,334,673 discloses a golf ball cover made from a composition of a polyurethane prepolymer and a slow-reacting polyamine curing agent and/or a difunctional glycol. Resultant golf balls are found to have improved shear

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resistance and cut resistance compared to covers made from balata or SURLYN®.

U.S. Pat. No. 5,692,974 discloses methods of using cationic ionomers in golf ball cover compositions. Additionally, the patent relates to golf balls having covers and cores incorporating urethane ionomers. Improved resiliency and initial velocity are achieved by the addition of an alkylating agent such as *t*-butyl-chloride which induces ionic interactions in the polyurethane to produce cationic type ionomers.

International patent application WO 98/37929 discloses a composition for golf ball covers that comprises a blend of a diisocyanate/polyol prepolymer and a curing agent comprising a blend of a slow-reacting diamine and a fast-reacting diamine. Improved "feel", playability, and durability characteristics are exhibited.

Conventional polyurethane elastomers are known to have lower resiliency than SURLYN® and other ionomer resins. It has now been discovered that the use of a polyurethane composition, according to the present invention, in forming golf ball cores, intermediate and mantle layers, and/or covers, can raise the velocity of a golf ball prepared with the composition: (1) closer to the velocities observed with SURLYN®-covered golf balls; and (2) higher than the velocities exhibited using alternative urethane compositions. Additionally, it is desired to combine polyurethane cover compositions with polybutadiene core materials, especially those having resilience indices greater than about 40. Cores formed of materials such as these have been found to provide exceptional resiliency characteristics without a loss in performance characteristics (i.e., decreased compression).

It is thus desired to prepare golf balls having lower compression, i.e., a softer ball, while having the same or higher resilience than conventional balls. It is alternatively desired to obtain the same or lower compression while achieving greater resilience.

SUMMARY OF THE INVENTION

The present invention is directed to a golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 200,000 and a resilience index of at least about 40; and a cover layer comprising a polyurethane composition formed from a prepolymer having no greater than 7.5 percent by weight unreacted isocyanate groups. Preferably, the resilience index is greater than about 50.

The prepolymer may include an isocyanate, at least one polyol, and at least one curing agent. Preferably, the isocyanate includes 4,4'-diphenylmethane diisocyanate, polymeric 4,4'-diphenylmethane diisocyanate, carbodimide-modified liquid 4,4'-diphenylmethane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, *p*-phenylene diisocyanate, toluene diisocyanate, isophoronediiisocyanate, *p*-methylxylene diisocyanate, *m*-methylxylene diisocyanate, *o*-methylxylene diisocyanate, or a mixture thereof. The at least one polyol may include polyether polyols, hydroxy-terminated polybutadiene, polyester polyols, polycaprolactone polyols, polycarbonate polyols, and mixtures thereof. The curing agent may include a polyamine curing agent, a polyol curing agent, or a mixture thereof. It is preferred, however, that the curing agent is a polyamine curing agent.

If the polyamine is selected as the curing agent, the polyamine curing agent may include 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof; 4,4'-bis-(*sec*-butylamino)-diphenylmethane; 1,4-bis-(*sec*-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol-di-*p*-

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aminobenzoate; polytetramethyleneoxide-di-*p*-aminobenzoate; *N,N'*-dialkyldiamino diphenyl methane; *p,p'*-methylene dianiline; phenylenediamine; 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); and mixtures thereof.

In one embodiment, however, the curing agent is a polyol curing agent. If the curing agent is a polyol, preferably, the polyol curing agent includes ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis-(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β -hydroxyethyl)ether; hydroquinone-di-(β -hydroxyethyl) ether; trimethylol propane, and mixtures thereof.

In another embodiment, the prepolymer has between about 2.5 percent and about 7.5 percent by weight unreacted isocyanate groups. The cover layer preferably has a thickness of less than about 0.05 inches. Further, the center should have a Mooney viscosity of between about 40 and about 80 and, preferably, between about 45 and about 60. In a preferred embodiment, the polybutadiene has a vinyl-polybutadiene isomer content of less than about 2 percent by weight and the polybutadiene has a *cis*-isomer content of at least about 95 percent by weight.

The golf ball center outer diameter is preferably of no less than about 1.55 inches and, additionally, the center further includes a material formed from a conversion reaction of polybutadiene having a first amount of *trans*-polybutadiene, a free radical source, and at least one *cis*-to-*trans* catalyst. Preferably, the reaction occurs at a temperature sufficient to form a polybutadiene reaction product having a second amount of *trans*-polybutadiene greater than the first amount of *trans*-polybutadiene. The *cis*-to-*trans* catalyst may include at least one of a organosulfur component, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound. The organosulfur component may include at least one of 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide. Preferably, the *cis*-to-*trans* catalyst is present in an amount from about 0.1 to 10 parts per hundred of polybutadiene.

In another embodiment, the golf ball further includes an intermediate layer juxtaposed between the center and the cover layer, wherein the intermediate layer comprises a material formed from a conversion reaction of polybutadiene having a first amount of *trans*-polybutadiene, a free radical source, and a *cis*-to-*trans* catalyst comprising at least one organosulfur component, wherein the intermediate layer has an outer diameter of no less than about 1.58 inches, and wherein the center has an outer diameter of less than about 1.55 inches. In yet another embodiment, the cover layer comprises an inner cover layer and an outer cover layer, the inner cover layer juxtaposed the center and the outer cover layer. Preferably, at least one of the inner and outer cover layer has a thickness of less than about 0.05 inches.

If present, the inner cover layer is formed from at least one material selected from the group comprising of an ionomer resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer,

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nylon, acrylonitrile butadiene-styrene copolymer or blends thereof. In still another embodiment, the inner cover has an outer diameter of at least about 1.55 inches and, preferably, between about 1.58 and about 1.64 inches. In an additional embodiment, the polyurethane is a thermoplastic or thermoset material.

The present invention is also directed to a golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 300,000 and a resilience index of at least about 40; an outer core layer having an outer diameter of no less than about 1.51 inches; an inner cover layer surrounding the outer core layer; and an outer cover layer comprising of a polyurethane composition formed from a prepolymer having no greater than about 7.5 percent by weight unreacted isocyanate groups. Preferably, the resilience index is greater than about 50.

The prepolymer may include an isocyanate, at least one polyol, and at least one curing agent. Preferably, the isocyanate includes 4,4'-diphenylmethane diisocyanate, polymeric 4,4'-diphenylmethane diisocyanate, carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, p-phenylene diisocyanate, toluene diisocyanate, isophoronediiisocyanate, p-methylxylene diisocyanate, m-methylxylene diisocyanate, o-methylxylene diisocyanate, or a mixture thereof. The at least one polyol may include polyether polyols, hydroxy-terminated polybutadiene, polyester polyols, polycaprolactone polyols, polycarbonate polyols, and mixtures thereof. The curing agent may include a polyamine curing agent, a polyol curing agent, or a mixture thereof. It is preferred, however, that the curing agent is a polyamine curing agent.

If the polyamine is selected as the curing agent, the polyamine curing agent may include 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, 3,5-diethyltoluene-2,4-diamine and isomers thereof, 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; 4,4'-methylene dianiline; phenylenediamine; 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); and mixtures thereof.

In one embodiment, however, the curing agent is a polyol curing agent. If the curing agent is a polyol, preferably, the polyol curing agent includes ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(hydroxyethyl)ether; hydroquinone-di-(hydroxyethyl)ether; trimethylol propane, and mixtures thereof.

In another embodiment, the prepolymer has between about 2.5 percent and about 7.5 percent by weight unreacted isocyanate groups. At least one of the inner and outer cover layers preferably has a thickness of less than about 0.05 inches. Further, the center should have a Mooney viscosity of between about 40 and about 80. In a preferred embodiment, the polybutadiene has a vinyl-polybutadiene isomer content of less than about 2 percent by weight and the polybutadiene has a cis-isomer content of at least about 95 percent by weight.

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The golf ball center outer diameter is preferably of no less than about 1.55 inches and, additionally, the center further includes a material formed from a conversion reaction of polybutadiene having a first amount of trans-polybutadiene, a free radical source, and at least one cis-to-trans catalyst. Preferably, the reaction occurs at a temperature sufficient to form a polybutadiene reaction product having an second amount of trans-polybutadiene greater than the first amount of trans-polybutadiene. The cis-to-trans catalyst may include at least one of an organosulfur compound, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound. The organosulfur component may include at least one of 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide. Preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 10 parts per hundred of polybutadiene.

In one embodiment, the inner cover layer includes an ionomer resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer nylon, acrylonitrile butadiene-styrene copolymer or blends thereof. The inner cover may have an outer diameter of at least about 1.55 inches and, preferably, between about 1.58 and about 1.64 inches. In an additional embodiment, the polyurethane is a thermoplastic or thermoset material.

The present invention is also directed to a golf ball comprising a center formed of a cis-polybutadiene having a molecular weight of greater than 300,000 and a resilience index of at least about 40; an outer core layer having an outer diameter of no less than about 1.51 inches; an inner cover layer surrounding the outer core layer, the inner cover layer comprising a polyurethane; and an outer cover layer comprising an ionomer or an elastomeric material.

The present invention is also directed to a golf ball comprising a center comprising a polybutadiene having a molecular weight of greater than 300,000 and a resilience index of at least about 40; an outer core layer having an outer diameter of no less than about 1.51 inches; an inner cover layer surrounding the outer core layer; and an outer cover layer; wherein the inner and outer cover layers are formed of a polyurethane composition.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a two-piece golf ball having a cover and a core according to the invention;

FIG. 2 is a cross-section of a golf ball having an intermediate layer between a cover and a center according to the invention; and

FIG. 3 is a cross-section of a golf ball having more than one intermediate layer between a cover and a center according to the invention.

DEFINITIONS

The term "about," as used herein in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range.

As used herein, "cis-to-trans catalyst" means any component or a combination thereof that will convert at least a portion of cis-polybutadiene isomer to trans-polybutadiene isomer at a given temperature. It should be understood that the combination of the cis-isomer, the trans-isomer, and any

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vinyl-isomer, measured at any given time, comprises 100 percent of the polybutadiene.

As used herein, the term "active ingredients" is defined as the specific components of a mixture or blend that are essential to the chemical reaction.

As used herein, substituted and unsubstituted "aryl" groups means a hydrocarbon ring bearing a system of conjugated double bonds, typically comprising $4n+2$ ring electrons, where n is an integer. Examples of aryl groups include, but are not limited to phenyl, naphthyl, anisyl, tolyl, xylenyl and the like. According to the present invention, aryl also includes heteroaryl groups, e.g., pyrimidine or thiophene. These aryl groups may also be substituted with any number of a variety of functional groups. In addition to the functional groups described herein in connection with carbocyclic groups, functional groups on the aryl groups can include hydroxy and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carboxyl including esters, acids, and metal salts thereof; silyl; acrylates and metal salts thereof; sulfonyl or sulfonamide; and phosphates and phosphites; and a combination thereof.

As used herein, the term "Atti compression" is defined as the deflection of an object or material relative to the deflection of a calibrated spring, as measured with an Atti Compression Gauge, that is commercially available from Atti Engineering Corp. of Union City, N.J. Atti compression is typically used to measure the compression of a golf ball. When the Atti Gauge is used to measure cores having a diameter of less than 1.680 inches, it should be understood that a metallic or other suitable shim is used to make the measured object 1.680 inches in diameter. However, when referring to the compression of a core, it is preferred to use a compressive load measurement. The term "compressive load" is defined as the normalized load in pounds for a 10.8-percent diametrical deflection for a spherical object having a diameter of 1.58 inches.

As used herein, substituted and unsubstituted "carbocyclic" means cyclic carbon-containing compounds, including, but not limited to cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, and the like. Such cyclic groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups having from 1-28 carbon atoms. The cyclic groups of the invention may further comprise a heteroatom.

As used herein, the term "coefficient of restitution" for golf balls is defined as the ratio of the rebound velocity to the inbound velocity when balls are fired into a rigid plate. The inbound velocity is understood to be 125 ft/s.

As used herein, the term "dynamic stiffness" is defined as load divided by the deflection for a 1.4-mm spherical radius penetration probe oscillating at 1 Hz with an amplitude of 100 μ m. The probe dynamically penetrates the surface of a sample material. Material samples of spherical cores were prepared by sectioning out a 6-mm-thick layer along the equator of core to produce a disk 6 mm thick with one surface containing the geometric center of the core. By positioning the probe at any selected radial position on the disk, a dynamic stiffness measurement may be obtained. Accurate dynamic measurements may be made by keeping the material sample at a substantially uniform temperature. The dynamic stiffness was acquired using a Dynamic Mechanical Analyzer, Model DMA 2980 available from TA Instruments Corporation of New Castle, Del. The instrument setting for the DMA 2980 were 1-Hz frequency, 100 μ m

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amplitude, 0.3-N static load, and auto strain of 105 percent. The 1.4-mm spherical radius probe is available from TA Instruments as a penetration kit accessory to the DMA 2980. The DMA 2980 is equipped with a temperature-controlled chamber that enables testing at a wide variety of ambient temperatures.

The method and instrument utilized for measuring "dynamic stiffness" may also be used to measure loss tangent (also commonly referred to as $\tan \delta$). Loss tangent is the ratio of loss modulus to storage modulus. Loss modulus is the portion of modulus which is out of phase with displacement and storage modulus is the portion of modulus which is in phase with displacement. The DMA 2980 automatically calculates and reports loss tangent.

As used herein, the terms "Group VIA component" or "Group VIA element" mean a component that includes a sulfur component, a selenium component, or a tellurium component, or a combination thereof.

As used herein, the term "sulfur component" means a component that is elemental sulfur, polymeric sulfur, or a combination thereof. It should be further understood that "elemental sulfur" refers to the ring structure of S_8 and that "polymeric sulfur" is a structure including at least one additional sulfur relative to the elemental sulfur.

As used herein, the term "fluid" includes a liquid, a paste, a gel, a gas, or any combination thereof.

As used herein, the term "molecular weight" is defined as the absolute weight average molecular weight. The molecular weight is determined by the following method: approximately 20 mg of polymer is dissolved in 10 mL of tetrahydrofuran ("THF"), which may take a few days at room temperature depending on the polymer's molecular weight and distribution. One liter of THF is filtered and degassed before being placed in a high-performance liquid chromatography ("HPLC") reservoir. The flow rate of the HPLC is set to 1 mL/min through a Viscogel column. This non-shedding, mixed bed, column model GMH_{HR}-H, which has an ID of 7.8 mm and 300 mm long is available from Viscotek Corp. of Houston, Tex. The THF flow rate is set to 1 mL/min for at least one hour before sample analysis is begun or until stable detector baselines are achieved. During this purging of the column and detector, the internal temperature of the Viscotek TDA Model 300 triple detector should be set to 40° C. This detector is also available from Viscotek Corp. The three detectors (i.e., Refractive Index, Differential Pressure, and Light Scattering) and the column should be brought to thermal equilibrium, and the detectors should be purged and zeroed, to prepare the system for calibration according to the instructions provided with this equipment. A 100- μ L aliquot of sample solution can then be injected into the equipment and the molecular weight of each sample can be calculated with the Viscotek's triple detector software. When the molecular weight of the polybutadiene material is measured, a dn/dc of 0.130 should always be used. It should be understood that this equipment and these methods provide the molecular weight numbers described and claimed herein, and that other equipment or methods will not necessarily provide equivalent values as used herein.

As used herein, the term "multilayer" means at least two layers and includes liquid center balls, wound balls, hollow-center balls, and balls with at least two intermediate layers and/or an inner or outer cover.

As used herein, the term "parts per hundred," also known as "phr," is defined as the number of parts by weight of a particular component present in a mixture, relative to 100

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parts by weight of the total polymer component. Mathematically, this can be expressed as the weight of an ingredient divided by the total weight of the polymer, multiplied by a factor of 100.

As used herein, the term "substantially free" means less than about 5 weight percent, preferably less than about 3 weight percent, more preferably less than about 1 weight percent, and most preferably less than about 0.01 weight percent.

As used herein the term "resilience index" is defined as the difference in loss tangent measured at 10 cpm and 1000 cpm divided by 990 (the frequency span) multiplied by 100,000 (for normalization and unit convenience). The loss tangent is measured using an RPA 2000 manufactured by Alpha Technologies of Akron, Ohio. The RPA 2000 is set to sweep from 2.5 to 1000 cpm at a temperature of 100° C. using an arc of 0.5 degrees. An average of six loss tangent measurements were acquired at each frequency and the average is used in calculation of the resilience index. The computation of resilience index is as follows:

$$\text{Resilience Index} = 100,000 \left[\frac{(\text{loss tangent @ 10 cpm}) - (\text{loss tangent @ 1000 cpm})}{990} \right]$$

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, a golf ball 10 of the present invention can include a core 12, a cover 16, and optional inner cover layer 16a surrounding the core 12. Referring to FIG. 2, a golf ball 20 of the present invention can include a center 22, a cover 26, an inner cover layer 26a, and at least one intermediate layer 24 disposed between the cover and the center. Each of the cover and center may also include more than one layer; i.e., the golf ball can be a conventional three-piece wound ball, a two-piece ball, a ball having a multi-layer core or an intermediate layer or layers, etc. Thus, referring to FIG. 3, a golf ball 30 of the present invention can include a center 32, a cover 38, and intermediate layers 34 and 36 disposed between the cover and the center. Although FIG. 3 shows only two intermediate layers, it will be appreciated that any number or type of intermediate layers may be used, as desired.

The present invention relates to two piece golf balls having a core and a cover, or multilayer golf balls having a solid, hollow, or fluid-filled center, a cover, and at least one intermediate layer disposed concentrically adjacent to the center. At least one of the center or optional intermediate layer includes a reaction product that includes a cis-to-trans catalyst, a resilient polymer component having polybutadiene, a free radical source, and optionally, a crosslinking agent, a filler, or both. Preferably, the reaction product has a first dynamic stiffness measured at -50° C that is less than about 130 percent of a second dynamic stiffness measured at 0° C. More preferably, the first dynamic stiffness is less than about 125 percent of the second dynamic stiffness. Most preferably, the first dynamic stiffness is less than about 110 percent of the second dynamic stiffness.

The invention also includes a method to convert the cis-isomer of the polybutadiene resilient polymer component to the trans-isomer during a molding cycle and to form a golf ball. Various combinations of polymers, cis-to-trans catalysts, fillers, crosslinkers, and a source of free radicals, may be used. To obtain a higher resilience and lower compression center or intermediate layer, a high-molecular weight polybutadiene with a cis-isomer content preferably greater than about 90 percent is converted to increase the

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percentage of trans-isomer content at any point in the golf ball or portion thereof, preferably to increase the percentage throughout substantially all of the golf ball or portion thereof, during the molding cycle. More preferably, the cis-polybutadiene isomer is present in an amount of greater than about 95 percent of the total polybutadiene content. Without wishing to be bound by any particular theory, it is believed that a low amount of 1,2-polybutadiene isomer ("vinyl-polybutadiene") is desired in the initial polybutadiene, and the reaction product. Typically, the vinyl polybutadiene isomer content is less than about 7 percent. Preferably, the vinyl polybutadiene isomer content is less than about 4 percent. More preferably, the vinyl polybutadiene isomer content is less than about 2 percent. Without wishing to be bound by any particular theory, it is also believed that the resulting mobility of the combined cis- and trans-polybutadiene backbone is responsible for the lower modulus and higher resilience of the reaction product and golf balls including the same.

To produce a polymer reaction product that exhibits the higher resilience and lower modulus (low compression) properties that are desirable and beneficial to golf ball playing characteristics, high-molecular-weight cis-1,4-polybutadiene, preferably may be converted to the trans-isomer during the molding cycle. The polybutadiene material typically has a molecular weight of greater than about 200,000. Preferably, the polybutadiene molecular weight is greater than about 250,000, more preferably between about 300,000 and 500,000. Without wishing to be bound by any particular theory, it is believed that the cis-to-trans catalyst component, in conjunction with the free radical source, acts to convert a percentage of the polybutadiene polymer component from the cis- to the trans-conformation. The cis-to-trans conversion requires the presence of a cis-to-trans catalyst, such as an organosulfur or metal-containing organosulfur compound, a substituted or unsubstituted aromatic organic compound that does not contain sulfur or metal, an inorganic sulfide compound, an aromatic organometallic compound, or mixtures thereof. The cis-to-trans catalyst component may include one or more of the other cis-to-trans catalysts described herein.

In one embodiment, the at least one organosulfur component is substantially free of metal, which typically means less than about 10 weight percent metal, preferably less than about 3 weight percent metal, more preferably less than about 1 weight percent metal, and most preferably only trace amounts of metal, such as less than about 0.01 weight percent.

As used herein when referring to the invention, the term "organosulfur compound(s)" or "organosulfur component(s)," means at least one of 4,4'-diphenyl disulfide; 4,4'-ditolyl disulfide; 2,2'-benzamido diphenyl disulfide; bis(2-aminophenyl)disulfide; bis(4-aminophenyl)disulfide; bis(3-aminophenyl)disulfide; 2,2'-bis(4-aminonaphthyl)disulfide; 2,2'-bis(3-aminonaphthyl)disulfide; 2,2'-bis(4-aminonaphthyl)disulfide; 2,2'-bis(5-aminonaphthyl)disulfide; 2,2'-bis(6-aminonaphthyl)disulfide; 2,2'-bis(7-aminonaphthyl)disulfide; 2,2'-bis(8-aminonaphthyl)disulfide; 1,1'-bis(2-aminonaphthyl)disulfide; 1,1'-bis(3-aminonaphthyl)disulfide; 1,1'-bis(4-aminonaphthyl)disulfide; 1,1'-bis(5-aminonaphthyl)disulfide; 1,1'-bis(6-aminonaphthyl)disulfide; 1,1'-bis(7-aminonaphthyl)disulfide; 1,1'-bis(8-aminonaphthyl)disulfide; 1,2'-diamino-1,2'-dithiodinaphthalene; 2,3'-diamino-1,2'-dithiodinaphthalene; bis(4-chlorophenyl)disulfide; bis(2-chlorophenyl)disulfide; bis(3-chlorophenyl)disulfide; bis(4-bromophenyl)disulfide;

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bis(2-bromophenyl)disulfide; bis(3-bromophenyl)disulfide; bis(4-fluorophenyl)disulfide; bis(4-iodophenyl)disulfide; bis(2,5-dichlorophenyl)disulfide; bis(3,5-dichlorophenyl)disulfide; bis(2,4-dichlorophenyl)disulfide; bis(2,6-dichlorophenyl)disulfide; bis(2,5-dibromophenyl)disulfide; bis(3,5-dibromophenyl)disulfide; bis(2-chloro-5-bromophenyl)disulfide; bis(2,4,6-trichlorophenyl)disulfide; bis(2,3,4,5,6-pentachlorophenyl)disulfide; bis(4-cyanophenyl)disulfide; bis(2-cyanophenyl)disulfide; bis(4-nitrophenyl)disulfide; bis(2-nitrophenyl)disulfide; 2,2'-dithiobenzoic acid ethylester; 2,2'-dithiobenzoic acid methylester; 2,2'-dithiobenzoic acid; 4,4'-dithiobenzoic acid ethylester; bis(4-acetylphenyl)disulfide; bis(2-acetylphenyl)disulfide; bis(4-formylphenyl)disulfide; bis(4-carbamoylphenyl)disulfide; 1,1'-dinaphthyl disulfide; 2,2'-dinaphthyl disulfide; 1,2'-dinaphthyl disulfide; 2,2'-bis(1-chlorodinaphthyl)disulfide; 2,2'-bis(1-bromodinaphthyl)disulfide; 1,1'-bis(2-chlorodinaphthyl)disulfide; 2,2'-bis(1-cyanodinaphthyl)disulfide; 2,2'-bis(1-acetylnaphthyl)disulfide; and the like; or a mixture thereof. Preferred organosulfur components include 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide, or a mixture thereof. A more preferred organosulfur component includes 4,4'-ditolyl disulfide. The organosulfur cis-to-trans catalyst, when present, is preferably present in an amount sufficient to produce the reaction product so as to contain at least about 12 percent trans-polybutadiene isomer, but typically is greater than about 32 percent trans-polybutadiene isomer based on the total resilient polymer component. Suitable metal-containing organosulfur components include, but are not limited to, cadmium, copper, lead, and tellurium analogs of diethyldithiocarbamate, diamylthiocarbamate, and dimethyldithiocarbamate, or mixtures thereof. Suitable substituted or unsubstituted aromatic organic components that do not include sulfur or a metal include, but are not limited to, 4,4'-diphenyl acetylene, azobenzene, or a mixture thereof. The aromatic organic group preferably ranges in size from C₆ to C₁₀, and more preferably from C₆ to C₁₀. Suitable inorganic sulfide components include, but are not limited to titanium sulfide, manganese sulfide, and sulfide analogs of iron, calcium, cobalt, molybdenum, tungsten, copper, selenium, yttrium, zinc, tin, and bismuth. The cis-to-trans catalyst may also be a blend of an organosulfur component and an inorganic sulfide component.

A substituted or unsubstituted aromatic organic compound may also be included in the cis-to-trans catalyst. In one embodiment, the aromatic organic compound is substantially free of metal. Suitable substituted or unsubstituted aromatic organic components include, but are not limited to, components having the formula (R₁)_x—R₃—M—R₄—(R₂)_y, wherein R₁ and R₂ are each hydrogen or a substituted or unsubstituted C₁₋₂₀ linear, branched, or cyclic alkyl, alkoxy, or alkylthio group, or a single, multiple, or fused ring C₆ to C₂₄ aromatic group; x and y are each an integer from 0 to 5; R₃ and R₄ are each selected from a single, multiple, or fused ring C₆ to C₂₄ aromatic group; and M includes an azo group or a metal component. R₃ and R₄ are each preferably selected from a C₆ to C₁₀ aromatic group, more preferably selected from phenyl, benzyl, naphthyl, benzamido, and benzothiazyl. R₁ and R₂ are each preferably selected from a substituted or unsubstituted C₁₋₁₀ linear, branched, or cyclic alkyl, alkoxy, or alkylthio group or a C₆ to C₁₀ aromatic group. When R₁, R₂, R₃, or R₄ are substituted, the substitution may include one or more of the following substituent groups: hydroxy and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carboxyl including esters, acids, and metal salts thereof;

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silyl; acrylates and metal salts thereof; sulfonyl or sulfonamide; and phosphates and phosphites. When M is a metal component, it may be any suitable elemental metal available to those of ordinary skill in the art. Typically, the metal will be a transition metal, although preferably it is tellurium or selenium.

The cis-to-trans catalyst can also include a Group VIA component, as defined herein. Elemental sulfur and polymeric sulfur are commercially available from, e.g., Elastochem, Inc. of Chardon, Ohio. Exemplary sulfur catalyst compounds include PB(RM-S)-80 elemental sulfur and PB(CRST)-65 polymeric sulfur, each of which is available from Elastochem, Inc. An exemplary tellurium catalyst under the tradename TELLOY and an exemplary selenium catalyst under the tradename VANDEX are each commercially available from RT Vanderbilt.

The cis-to-trans catalyst is preferably present in an amount from about 0.1 to 10 parts per hundred of the total resilient polymer component. More preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 5 parts per hundred of the total resilient polymer component. Most preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 8 parts per hundred of the total resilient polymer component. The cis-to-trans catalyst is typically present in an amount sufficient to produce the reaction product so as to increase the trans-polybutadiene isomer content to contain from about 5 percent to 70 percent trans-polybutadiene based on the total resilient polymer component.

The measurement of trans-isomer content of polybutadiene referred to herein was and can be accomplished as follows. Calibration standards are prepared using at least two polybutadiene rubber samples of known trans-content, e.g., high and low percent trans-polybutadiene. These samples are used alone and blended together in such a way as to create a ladder of trans-polybutadiene content of at least about 1.5% to 50% or to bracket the unknown amount, such that the resulting calibration curve contains at least about 13 equally spaced points.

Using a commercially available Fourier Transform Infrared ("FTIR") spectrometer equipped with a Photoacoustic ("PAS") cell, a PAS spectrum of each standard was obtained using the following instrument parameters: scan at speed of 2.5 KHz (0.16 cm/s optical velocity), use a 1.2 KHz electronic filter, set an undersampling ratio of 2 (number of laser signal zero crossings before collecting a sample), co-add a minimum of 128 scans at a resolution of 4 cm⁻¹ over a range of 375 to 4000 cm⁻¹ with a sensitivity setting of 1.

The cis-, trans-, and vinyl-polybutadiene peaks are typically found between 600 and 1100 cm⁻¹ in the PAS spectrum. The area under each of the trans-polybutadiene peaks can be integrated. Determining the fraction of each peak area relative to the total area of the three isomer peaks allow construction of a calibration curve of the trans-polybutadiene area fraction versus the actual trans-polybutadiene content. The correlation coefficient (R²) of the resulting calibration curve must be a minimum of 0.95.

A PAS spectrum is obtained, using the parameters described above, for the unknown core material at the point of interest (e.g., the surface or center of the core) by filling the PAS cell with a sample containing a freshly cut, uncontaminated surface free of foreign matters, such as mold release and the like. The trans-polybutadiene area fraction of the unknown is analyzed to determine the actual trans-isomer content from the calibration curve.

In one known circumstance when barium sulfate is included, the above method for testing trans-content may be

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less accurate. Thus, an additional or alternative test of the trans-content of polybutadiene is as follows. Calibration standards are prepared using at least two polybutadienes of known trans-content (e.g., high and low percent trans-polybutadiene). These samples are used alone and blended together in such a way as to create a ladder of trans-polybutadiene content of at least about 1.5% to 50% or to bracket the unknown amount, such that the resulting calibration curve contains at least about 13 equally spaced points.

Using a Fourier Transform Raman ("FT-Raman") spectrometer equipped with a near-infrared laser, a Stokes Raman spectrum should be obtained from each standard using the following instrument parameters: sufficient laser power to obtain a good signal-to-noise ratio ("S/N") without causing excessive heating or fluorescence (typically about 400 to 800 mW is suitable); a resolution of 2 cm^{-1} ; over a Raman shift spectral range of about 400 to 4000 cm^{-1} ; and co-adding at least 300 scans.

A calibration curve may be constructed from the data generated above, using a chemometrics approach and software such as PLSplus/IQ from Galactic Industries Corp. of Salem, N.H. An acceptable calibration was obtained with this software using a PLS-1 curve generated using an SNV (detrend) pathlength correction, a mean center data preparation, and a 5-point SG second derivative over the spectral range from about 1600 to 1700 cm^{-1} . The correlation coefficient (R^2) of the resulting calibration curve must be a minimum of 0.95.

A Raman spectrum of the core material is obtained using this instrument at the point of interest in the sample (e.g., surface or center of the golf ball core). The sample must be free of foreign matter, such as mold release, etc. Analyze the spectrum of the sample using the PLS calibration curve to determine trans-polybutadiene isomer content of the sample.

A free-radical source, often alternatively referred to as a free-radical initiator, is required in the composition and method. The free-radical source is typically a peroxide, and preferably an organic peroxide. Suitable free-radical sources include di-*t*-amyl peroxide, di(2-*t*-butyl-peroxyisopropyl) benzene peroxide, 1,1-bis(*t*-butylperoxy)-3,3,5-trimethylcyclohexane, dicumyl peroxide, di-*t*-butyl peroxide, 2,5-di-(*t*-butylperoxy)-2,5-dimethyl hexane, *n*-butyl-4,4-bis(*t*-butylperoxy)valerate, lauryl peroxide, benzoyl peroxide, *t*-butyl hydroperoxide, and the like, and any mixture thereof. The peroxide is typically present in an amount greater than about 0.1 parts per hundred of the total resilient polymer component, preferably about 0.1 to 15 parts per hundred of the resilient polymer component, and more preferably about 0.2 to 5 parts per hundred of the total resilient polymer component. It should be understood by those of ordinary skill in the art that the presence of certain *cis*-to-*trans* catalysts according to the invention may require a larger amount of free-radical source, such as the amounts described herein, compared to conventional cross-linking reactions. The free radical source may alternatively or additionally be one or more of an electron beam, UV or gamma radiation, x-rays, or any other high energy radiation source capable of generating free radicals. It should be further understood that heat often facilitates initiation of the generation of free radicals.

Crosslinkers are included to increase the hardness of the reaction product. Suitable crosslinking agents include one or more metallic salts of unsaturated fatty acids or monocarboxylic acids, such as zinc, calcium, or magnesium acrylate salts, and the like, and mixtures thereof. Preferred acrylates

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include zinc acrylate, zinc diacrylate, zinc methacrylate, and zinc dimethacrylate, and mixtures thereof. The crosslinking agent must be present in an amount sufficient to crosslink a portion of the chains of polymers in the resilient polymer component. For example, the desired compression may be obtained by adjusting the amount of crosslinking. This may be achieved, for example, by altering the type and amount of crosslinking agent, a method well-known to those of ordinary skill in the art. The crosslinking agent is typically present in an amount greater than about 0.1 percent of the resilient polymer component, preferably from about 10 to 40 percent of the resilient polymer component, more preferably from about 10 to 30 percent of the resilient polymer component. When an organosulfur is selected as the *cis*-to-*trans* catalyst, zinc diacrylate may be selected as the crosslinking agent and is present in an amount of less than about 25 phr.

Fillers added to one or more portions of the golf ball typically include processing aids or compounds to affect rheological and mixing properties, the specific gravity (i.e., density-modifying fillers), the modulus, the tear strength, reinforcement, and the like. The fillers are generally inorganic, and suitable fillers include numerous metals or metal oxides, such as zinc oxide and tin oxide, as well as barium sulfate, zinc sulfate, calcium carbonate, barium carbonate, clay, tungsten, tungsten carbide, an array of silicas, and mixtures thereof. Fillers may also include various foaming agents or blowing agents which may be readily selected by one of ordinary skill in the art. Polymeric, ceramic, metal, and glass microspheres may be solid or hollow, and filled or unfilled. Fillers are typically also added to one or more portions of the golf ball to modify the density thereof to conform to uniform golf ball standards. Fillers may also be used to modify the weight of the center or at least one additional layer for specialty balls, e.g., a lower weight ball is preferred for a player having a low swing speed.

The polymers, free-radical initiator, filler(s), and any other materials used in forming either the golf ball center or any portion of the core, in accordance with invention, may be combined to form a mixture by any type of mixing known to one of ordinary skill in the art. Suitable types of mixing include single pass and multi-pass mixing, and the like. The crosslinking agent, and any other optional additives used to modify the characteristics of the golf ball center or additional layer(s), may similarly be combined by any type of mixing. A single-pass mixing process where ingredients are added sequentially is preferred, as this type of mixing tends to increase efficiency and reduce costs for the process. The preferred mixing cycle is single step wherein the polymer, *cis*-*trans* catalyst, filler, zinc diacrylate, and peroxide are added sequentially. Suitable mixing equipment is well known to those of ordinary skill in the art, and such equipment may include a Banbury mixer, a two-roll mill, or a twin screw extruder. Conventional mixing speeds for combining polymers are typically used, although the speed must be high enough to impart substantially uniform dispersion of the constituents. On the other hand, the speed should not be too high, as high mixing speeds tend to break down the polymers being mixed and particularly may undesirably decrease the molecular weight of the resilient polymer component. The speed should thus be low enough to avoid high shear, which may result in loss of desirably high molecular weight portions of the polymer component. Also, too high a mixing speed may undesirably result in creation of enough heat to initiate the crosslinking before the pre-forms are shaped and assembled around a core. The mixing temperature depends upon the type of polymer components,

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and more importantly, on the type of free-radical initiator. For example, when using di(2-t-butyl-peroxyisopropyl) benzene as the free-radical initiator, a mixing temperature of about 80° C. to 125° C., preferably about 88° C. to 110° C., and more preferably about 90° C. to 100° C., is suitable to safely mix the ingredients. Additionally, it is important to maintain a mixing temperature below the peroxide decomposition temperature. For example, if dicumyl peroxide is selected as the peroxide, the temperature should not exceed 200° F. Suitable mixing speeds and temperatures are well-known to those of ordinary skill in the art, or may be readily determined without undue experimentation.

The mixture can be subjected to, e.g., a compression or injection molding process, to obtain solid spheres for the center or hemispherical shells for forming an intermediate layer. The polymer mixture is subjected to a molding cycle in which heat and pressure are applied while the mixture is confined within a mold. The cavity shape depends on the portion of the golf ball being formed. The compression and heat liberates free radicals by decomposing one or more peroxides, which may initiate the cis-to-trans conversion and crosslinking simultaneously. The temperature and duration of the molding cycle are selected based upon the type of peroxide and cis-trans catalyst selected. The molding cycle may have a single step of molding the mixture at a single temperature for a fixed time duration. An example of a single step molding cycle, for a mixture that contains dicumyl peroxide, would hold the polymer mixture at 340° F. for a duration of 15 minutes. The molding cycle may also include a two-step process, in which the polymer mixture is held in the mold at an initial temperature for an initial duration of time, followed by holding at a second, typically higher temperature for a second duration of time. An example of a two-step molding cycle would be holding the mold at 290° F. for 40 minutes, then ramping the mold to 340° F. where it is held for a duration of 20 minutes. In a preferred embodiment of the current invention, a single-step cure cycle is employed. Single-step processes are effective and efficient, reducing the time and cost of a two-step process. The resilient polymer component, polybutadiene, cis-to-trans conversion catalyst, additional polymers, free-radical initiator, filler, and any other materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a golf ball by an injection molding process, which is also well-known to one of ordinary skill in the art. Although the curing time depends on the various materials selected, a particularly suitable curing time is about 5 to 18 minutes, preferably from about 8 to 15 minutes, and more preferably from about 10 to 12 minutes. Those of ordinary skill in the art will be readily able to adjust the curing time upward or downward based on the particular materials used and the discussion herein.

The cured resilient polymer component, which contains a greater amount of trans-polybutadiene than the uncured resilient polymer component, is formed into an article having a first hardness at a point in the interior and a surface having a second hardness such that the second hardness differs from the first hardness by greater than 10 percent of the first hardness. Preferably, the article is a sphere and the point is the midpoint of the article. In another embodiment, the second hardness differs from the first by greater than 20 percent of the first hardness. The cured article also has a first amount of trans-polybutadiene at an interior location and a second amount of trans-polybutadiene at a surface location, wherein the first amount is at least about 6 percent less than the second amount, preferably at least about 10 percent less

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than the second amount, and more preferably at least about 20 percent less than the second amount. The interior location is preferably a midpoint and the article is preferably a sphere. The compression of the core, or portion of the core, of golf balls prepared according to the invention is preferably below about 50, more preferably below about 25.

The cover provides the interface between the ball and a club. Properties that are desirable for the cover are good moldability, high abrasion resistance, high tear strength, high resilience, and good mold release, among others. The cover typically has a thickness to provide sufficient strength, good performance characteristics and durability. The cover preferably has a thickness of less than about 0.1 inches, more preferably, less than about 0.05 inches, and most preferably, between about 0.02 and about 0.04 inches. The invention is particularly directed towards a multilayer golf ball which comprises a core, an inner cover layer, and an outer cover layer. In this embodiment, preferably, at least one of the inner and outer cover layers has a thickness of less than about 0.05 inches, more preferably between about 0.02 and about 0.04 inches. Most preferably, the thickness of either layer is about 0.03 inches.

When the golf ball of the present invention includes an intermediate layer, such as an inner cover layer, this layer can include any materials known to those of ordinary skill in the art, including thermoplastic and thermosetting materials, but preferably the intermediate layer can include any suitable materials, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid which are available under the trademark SURLYN of E.I. DuPont de Nemours & Co., of Wilmington, Del., or IOTEK or ESCOR of Exxon. These are copolymers or terpolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel or the like, in which the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include methacrylic, crotonic, maleic, fumaric or itaconic acid.

This golf ball can likewise include one or more homopolymeric or copolymeric intermediate materials, such as:

- (1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;
- (2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methylacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst;
- (3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates and those disclosed in U. S. Pat. No. 5,334,673;
- (4) Polyureas, such as those disclosed in U.S. Pat. No. 5,484,870;
- (5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly (caprolactam), and blends of polyamides with SURLYN, polyethylene, ethylene copolymers, ethylpropylene-non-conjugated diene terpolymer, and the like;

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- (6) Acrylic resins and blends of these resins with poly vinyl chloride, elastomers, and the like;
- (7) Thermoplastics, such as urethanes; olefinic thermoplastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer; block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly(ether-amide), such as PEBAX, sold by ELF Atochem of Philadelphia, Pa.;
- (8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene as sold under the trademark NORYL by General Electric Company of Pittsfield, Mass.;
- (9) Thermoplastic polyesters, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified and elastomers sold under the trademarks HYTREL by E.I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD by General Electric Company of Pittsfield, Mass.;
- (10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene or ethylene vinyl acetate or other elastomers; and
- (11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

Preferably, the optional intermediate layer includes polymers, such as ethylene, propylene, butene-1 or hexene-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. More preferably, in a low spin rate embodiment designed for maximum distance, the acrylic or methacrylic acid is present in about 15 to 35 weight percent, making the ionomer a high modulus ionomer. In a high spin embodiment, the cover includes an ionomer where an acid is present in about 10 to 15 weight percent and includes a softening comonomer.

The cover preferably include a polyurethane composition comprising the reaction product of at least one polyisocyanate, polyol, and at least one curing agent.

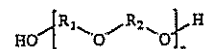
Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"), polymeric MDI, carbodiimide-modified liquid MDI, 4,4'-dicyclohexylmethane diisocyanate ("H₁₂MDI"), p-phenylene diisocyanate ("PPDI"), toluene diisocyanate

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("TDI"), 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"), isophoronediiisocyanate ("IPDI"), hexamethylene diisocyanate ("HDI"), naphthalene diisocyanate ("NDI"); xylene diisocyanate ("XDI"); para-tetramethylxylene diisocyanate ("p-TMXDI"); meta-tetramethylxylene diisocyanate ("m-TMXDI"); ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl-1,6-hexane diisocyanate ("TMDI"), tetracene diisocyanate, naphthalene diisocyanate, anthracene diisocyanate, and mixtures thereof. Polyisocyanates are known to those of ordinary skill in the art as having more than one isocyanate group, e.g., di-, tri-, and tetra-isocyanate. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term "MDI" includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 7.5% NCO, more preferably, between about 2.5% and about 7.5%, and most preferably, between about 4% to about 6.5%.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol, more preferably those polyols that have the generic structure:

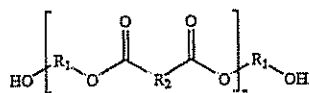


where R₁ and R₂ are straight or branched hydrocarbon chains, each containing from 1 to about 20 carbon atoms, and n ranges from 1 to about 45. Examples include, but are not limited to, polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

In another embodiment, polyester polyols are included in the polyurethane material of the invention. Preferred polyester polyols have the generic structure:

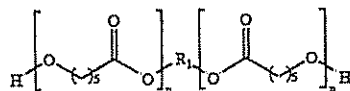
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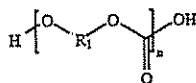
where R_1 and R_2 are straight or branched hydrocarbon chains, each containing from 1 to about 20 carbon atoms, and n ranges from 1 to about 25. Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol, polybutylene adipate glycol, polyethylene propylene adipate glycol, ortho-phthalate-1,6-hexanediol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In another embodiment, polycaprolactone polyols are included in the materials of the invention. Preferably, any polycaprolactone polyols have the generic structure:



where R_1 is a straight chain or branched hydrocarbon chain containing from 1 to about 20 carbon atoms, and n is the chain length and ranges from 1 to about 20. Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In yet another embodiment, the polycarbonate polyols are included in the polyurethane material of the invention. Preferably, any polycarbonate polyols have the generic structure:



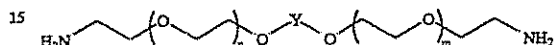
where R_1 is predominantly bisphenol A units $-(\text{p}-\text{C}_6\text{H}_4)-\text{C}(\text{CH}_3)_2-(\text{p}-\text{C}_6\text{H}_4)-$ or derivatives thereof, and n is the chain length and ranges from 1 to about 20. Suitable polycarbonates include, but are not limited to, polyphthalate carbonate. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups. In one embodiment, the molecular weight of the polyol is from about 200 to about 4000.

Polyamine curatives are also suitable for use in the polyurethane composition of the invention and have been found to improve cut, shear, and impact resistance of the resultant balls. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine ("MPDA"); 4,4'-methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-

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methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as ETHACURE 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives, which include both primary and secondary amines, preferably have molecular weights ranging from about 64 to about 2000.

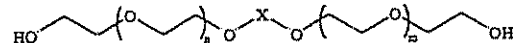
Other suitable polyamine curatives include those having the general formula:



where n and m each separately have values of 0, 1, 2, or 3, and where Y is 1,2-cyclohexyl, 1,3-cyclohexyl, 1,4-cyclohexyl, ortho-phenylene, meta-phenylene, or para-phenylene, or a combination thereof. Preferably, n and m , each separately, have values of 0, 1, or 2, and preferably, 1 or 2.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β -hydroxyethyl)ether; hydroquinone-di-(β -hydroxyethyl)ether; and mixtures thereof. Preferred hydroxy-terminated curatives include ethylene glycol; diethylene glycol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol, trimethylol propane, and mixtures thereof.

Preferably, the hydroxy-terminated curatives have molecular weights ranging, from about 48 to 2000. It should be understood that molecular weight, as used herein, is the absolute weight average molecular weight and would be understood as such by one of ordinary skill in the art. Other suitable hydroxy-terminated curatives have the following general chemical structure:



where n and m each separately have values of 0, 1, 2, or 3, and where X is ortho-phenylene, meta-phenylene, para-phenylene, 1,2-cyclohexyl, 1,3-cyclohexyl, or 1,4-cyclohexyl, or mixtures thereof. Preferably, n and m each separately have values of 0, 1, or 2, and more preferably, 1 or 2.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

Any method known to one of ordinary skill in the art may be used to combine the polyisocyanate, polyol, and curing agent of the present invention. One commonly employed

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method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogeneous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition.

An optional filler component may be chosen to impart additional density to blends of the previously described components. The selection of such filler(s) is dependent upon the type of golf ball desired (i.e., one-piece, two-piece multi-component, or wound). Examples of useful fillers include zinc oxide, barium sulfate, calcium oxide, calcium carbonate and silica, as well as the other well known corresponding salts and oxides thereof. Additives, such as nanoparticles, glass spheres, and various metals, such as titanium and tungsten, can be added to the polyurethane compositions of the present invention, in amounts as needed, for their well-known purposes. Additional components which can be added to the polyurethane composition include UV stabilizers and other dyes, as well as optical brighteners and fluorescent pigments and dyes. Such additional ingredients may be added in any amounts that will achieve their desired purpose.

Due to the very thin nature, it has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the urethane elastomer material can be applied over the inner core using a variety of application techniques such as spraying, dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Pat. No. 5,733,428, filed May 2, 1995 entitled "Method And Apparatus For Forming Polyurethane Cover On A Golf Ball", the disclosure of which is hereby incorporated by reference in its entirety in the present application.

The cover is preferably formed around the coated core by mixing and introducing the material in the mold halves. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing cores into the mold halves is determined to be approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using pins moving into holes in each mold. After the reacting materials have resided in top mold halves for about 50 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity.

A ball cup holds the ball core through reduced pressure (or partial vacuum) in hose. Upon location of the coated core in

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the halves of the mold after gelling for about 50 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit, inverted and mated with other mold halves which, at an appropriate time earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

Similarly, U.S. Pat. No. 5,006,297 to Brown et al. and U.S. Pat. No. 5,334,673 to Wu both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

Depending on the desired properties, balls prepared according to the invention can exhibit substantially the same or higher resilience, or coefficient of restitution ("COR"), with a decrease in compression or modulus, compared to balls of conventional construction. Additionally, balls prepared according to the invention can also exhibit substantially higher resilience, or COR, without an increase in compression, compared to balls of conventional construction. Another measure of this resilience is the "loss tangent," or $\tan \delta$, which is obtained when measuring the dynamic stiffness of an object. Loss tangent and terminology relating to such dynamic properties is typically described according to ASTM D4092-90. Thus, a lower loss tangent indicates a higher resiliency, thereby indicating a higher rebound capacity. Low loss tangent indicates that most of the energy imparted to a golf ball from the club is converted to dynamic energy, i.e., launch velocity and resulting longer distance. The rigidity or compressive stiffness of a golf ball may be measured, for example, by the dynamic stiffness. A higher dynamic stiffness indicates a higher compressive stiffness. To produce golf balls having a desirable compressive stiffness, the dynamic stiffness of the crosslinked reaction product material should be less than about 50,000 N/m at -50°C . Preferably, the dynamic stiffness should be between about 10,000 and 40,000 N/m at -50°C , more preferably, the dynamic stiffness should be between about 20,000 and 30,000 N/m at -50°C .

The dynamic stiffness is similar in some ways to dynamic modulus. Dynamic stiffness is dependent on probe geometry as described herein, whereas dynamic modulus is a unique material property, independent of geometry. The dynamic stiffness measurement has the unique attribute of enabling quantitative measurement of dynamic modulus and exact measurement of loss tangent at discrete points within a sample article. In the case of this invention, the article is a golf ball core. The polybutadiene reaction product preferably has a loss tangent below about 0.1 at -50°C , and more preferably below about 0.07 at -50°C .

The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression (which has been referred to as PGA compression in the past) of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball polybutadiene material of the present invention typically has a flexural modulus of from about 500 psi to 300,000 psi, preferably from about 2000 to 200,000 psi. The golf ball polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D. The specific gravity is typically greater than about 0.7,

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preferably greater than about 1, for the golf ball polybutadiene material.

The center composition should comprise at least one rubber material having a resilience index of at least about 40. Preferably the resilience index is at least about 50. A comparison of a number of polybutadiene polymers are listed in Table 1 below. Polymers that produce resilient golf balls and, therefore, are suitable for the present invention, include but are not limited to CB23, CB22, BR60, and 1207G. To clarify the method of computation for resilience index, the resilience index for CB23, for example, is computed as follows:

$$\text{Resilience Index for CB23} = 100,000 \cdot \{(0.954) - (0.407)\}^{990}$$

$$\text{Resilience Index for CB23} = 55$$

TABLE 1

Resilience Index of example polybutadiene polymers			
Rubber	Tnn δ at		Resilience Index at
	10 cpm	1000 cpm	100° C.
CB23	0.954	0.407	55
CB22	0.895	0.358	54
BR-60	0.749	0.350	40
BR-40	0.841	0.446	40
Takene 8855	0.720	0.414	31
CARIFLEX BR1220	0.487	0.439	5
BUDENE 1207G	0.825	0.388	44

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tion typically has a Mooney viscosity of between about 40 and about 80, more preferably, between about 45 and about 60, and most preferably, between about 45 and about 55. Mooney viscosity is typically measured according to ASTM D-1646.

When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 500 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-2240, between about 30 and about 60 Shore D, preferably from about 35 to about 55 Shore D. The inner cover layer, if present, preferably has a material hardness from about 50 to about 75 Shore D, preferably from about 60 to about 65 Shore D.

EXAMPLES

A variety of cores were prepared according to the present invention, as well as some cores prepared using conventional materials. All cores in Table 2 were prepared to a diameter of 1.58 inches. The recipes for each core, and values measured for compression and COR are presented in Table 2 below:

TABLE 2

Golf Ball Core Properties from Various Rubber Formulations						
Ingredients	Mooney viscosity @ 100° C.	1	2	3	4	5
CB23	51	100				
CB22	63		100			
BR-60	60			100		
Takene 8855	48				100	
CARIFLEX BR1220	43					100
zinc diacrylate		28	28	28	28	28
peroxide		0.53	0.53	0.53	0.53	0.53
zinc oxide		4.3	4.3	4.3	4.3	4.3
tungsten		11.0	11.0	11.0	11.0	11.0
Core Properties						
compression		77	75	77	76	71
COR @ 125 ft/s		0.815	0.811	0.810	0.807	0.802

The molding process and composition of golf ball portions typically results in a gradient of material properties. Methods employed in the prior art generally exploit hardness to quantify these gradients. Hardness is a qualitative measure of static modulus and does not represent the modulus of the material at the deformation rates associated with golf ball use, i.e., impact by a club. As is well known to one skilled in the art of polymer science, the time-temperature superposition principle may be used to emulate alternative deformation rates. For golf ball portions including polybutadiene, a 1-Hz oscillation at temperatures between 0° C. and -50° C. are believed to be qualitatively equivalent to golf ball impact rates. Therefore, measurement of loss tangent and dynamic stiffness at 0° C. to -50° C. may be used to accurately anticipate golf ball performance, preferably at temperatures between about -20° C. and -50° C.

Additionally, the unvulcanized rubber, such as polybutadiene, in golf balls prepared according to the inven-

A variety of metal sulfide cis-to-trans catalysts that successfully converted a portion of the cis-polybutadiene isomer to the trans-isomer are presented in Table 3. CARIFLEX BR1220 polybutadiene (100 phr) was reacted with zinc oxide (5 phr), dicumyl peroxide (3 phr, the free radical initiator), and zinc diacrylate (25 phr), to form the reaction product as described in the present invention.

Trans-isomer conversion percentages range from below 8 percent to above 17 percent for the various catalysts that are present in amounts ranging from below 1.7 phr to above 3.7 phr. The table clearly demonstrates the effectiveness of numerous different cis-to-trans catalysts, at varying concentrations, for increasing the trans-polybutadiene content.

[illegible]

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TABLE 4

	Invention			Examples of Conventional Golf Balls			
	Examples			U.S. Pat. No.	U.S. Pat. No.	U.S. Pat. No.	U.S. Pat. No.
	#1	#2	#3	3239228	5816944	5252652	4971329
<u>Chemical Constituents</u>					U.S. Pat. No. 5697856		U.S. Pat. No. 4692497
Polybutadiene (Shell, CARIFLEX BR1220)	100	100	100		N/A	N/A	N/A
Polybutadiene (Firestone, 35 NF)				100	N/A	N/A	N/A
DMDS				2.1	N/A	N/A	N/A
Carbon Black (RA)				15	N/A	N/A	N/A
Wood Flour				24	N/A	N/A	N/A
Sulfur				24	N/A	N/A	N/A
Stearic Acid				1.5	N/A	N/A	N/A
Reogen				15	N/A	N/A	N/A
Vanox MBPC				2	N/A	N/A	N/A
Triethanolamine				4	N/A	N/A	N/A
Zinc oxide	5	5	5	5	N/A	N/A	N/A
Dicumyl peroxide	3	1.9	2		N/A	N/A	N/A
Zinc Diacrylate	25	25	25		N/A	N/A	N/A
Cis-Trans "Catalyst"					N/A	N/A	N/A
MnS		0.82			N/A	N/A	N/A
Dithyldisulfide	2.5		1.5		N/A	N/A	N/A
Cu ₂ S			1		N/A	N/A	N/A
<u>Resultant Core Properties</u>							
Load (lbs) @ 10.8% Deflection 1.580" core	165.5	191.4	191.8	61.1	325	390	480
Coefficient of Restitution @ 125 ft/s	0.783	0.777	0.785	0.599	0.779	0.805	0.775
<u>Hardness Shore C</u>							
Surface	61	76	62	35	75	80	80.5
Center	52	52	59	30	70	61	66.5
<u>Dynamic Stiffness @ 0° C. (N/m)</u>							
Edge*	25338	27676	28493	8312	62757	83032	72235
Center	20783	17390	27579	8361	61071	26264	50612
<u>Dynamic Stiffness @ -50° C. (N/m)</u>							
Edge*	30265	34523	34455	19394	92763	109053	108242
Center	23022	20603	32195	18617	89677	28808	83183
<u>Dynamic Stiffness Ratio at -50° C./0° C.</u>							
Edge*	119%	125%	121%	233%	148%	131%	150%
Center	111%	118%	117%	223%	147%	110%	164%
<u>Loss Tangent 0° C.</u>							
Edge*	0.024	0.027	0.024	0.074	0.039	0.037	0.045
Center	0.025	0.023	0.023	0.073	0.033	0.025	0.043
<u>Loss Tangent -50° C.</u>							
Edge*	0.098	0.084	0.097	0.183	0.142	0.119	0.099
Center	0.067	0.071	0.085	0.180	0.129	0.059	0.095
% Trans BR isomer Precure	1.5	1.5	1.5	50	N/A	N/A	N/A
% Trans BR isomer Postcure							
Surface	55.8	8.4	45.5	50	30.2	24.6	1.5
Center	37.8	4.6	25.5	50	24.7	8.5	1.5
% Trans Variation (Surf. - Center)/ Surf.	32%	45%	44%	0%	18%	65%	0%

*Edge is measured approximately 5 mm from the exterior surface of the measured article.

Example 2

A Core Prepared From According to the Invention,
Employing an Inorganic Sulfide Cis-to-trans
Catalyst

A core according to the present invention was created employing an inorganic sulfide compound as the cis-to-trans conversion catalyst. The resultant core properties clearly demonstrate the advantages of a golf ball core made according to the current invention as compared to example cores constructed with conventional technology. The components and physical characteristics are presented in Table 4.

The compressive load is approximately half of the compressive load of three cores constructed in accordance with

U.S. Pat. Nos. 5,697,856, 5,252,652, and 4,692,497, while at the same time retaining roughly the same, and in some cases, a higher COR (resilience). The core made according to the current invention is soft, yet resilient (fast). The compressive load is greater than a core constructed in accordance with U.S. Pat. No. 3,239,228, but has a significantly higher COR. The core of U.S. Pat. No. 3,239,228 is very soft and very slow (low COR).

The percent change in dynamic stiffness from 0° C. to -50° C. was also measured at both the edge and center of the cores. The dynamic stiffness at both the edge and the center of the core of the current invention varied only slightly, less than 125 percent, over the temperature range investigated. The core made according to U.S. Pat. No. 3,239,228 varied over 230 percent, whereas the cores made according to other

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conventional technology, had a dynamic stiffness that varied by greater than 130 percent, and typically by as much as 150 percent, over the same temperature range.

The percent of trans-conversion was also measured at both the center and edge of the core prepared according to the current invention, and for cores prepared according to the same four patents mentioned above, allowing a trans-gradient to be calculated. The core according to the current invention had a trans-gradient of about 45 percent from edge to center. Two of the cores prepared in accordance with U.S. Pat. Nos. 3,239,228 and 4,692,497 had a zero trans-gradient. A third core, prepared in accordance with U.S. Pat. No. 5,697,856, had only a slight trans-gradient, less than 18 percent from edge to center. A fourth core, prepared in accordance with U.S. Pat. No. 5,252,652, had a very large gradient, almost 65 percent, from edge to center.

Example 3

A Core Prepared From According to the Invention,
Employing a Blend of Organosulfur and Inorganic
Sulfide Cis-to-trans Catalyst

A core according to the present invention was created employing a blend of organosulfur and inorganic sulfide compounds as the cis-to-trans conversion catalyst. The resultant core properties clearly demonstrate the advantages of a golf ball core made according to the current invention (is compared to example cores constructed with conventional technology. The components and physical characteristics are presented in Table 4.

The compressive load is approximately half of the compressive load of three cores constructed in accordance with U.S. Pat. Nos. 5,697,856, 5,252,652, and 4,692,497, while at the same time retaining roughly the same, and in some cases a higher COR (resilience). The core made according to the current invention is soft, yet resilient (fast). The compressive load of the invention is greater than a fourth core constructed in accordance with U.S. Pat. No. 3,239,228, but has a significantly higher COR. The core constructed in accordance with U.S. Pat. No. 3,239,228 is very soft and very slow (low COR).

The percent change in dynamic stiffness from 0° C. to -50° C. was also measured at both the edge and center of the cores. The dynamic stiffness at both the edge and the center of the core of the current invention varied only slightly, less than 121 percent, over the temperature range investigated. The core made in accordance with U.S. Pat. No. 3,239,228 varied over 230 percent, whereas the cores made according to other conventional technology had a dynamic stiffness that varied by greater than 130 percent, and typically by as much as 150 percent, over the same temperature range.

The percent of trans-conversion was also measured at both the center and edge of the core prepared according to the current invention, and for cores prepared to the same four patents mentioned above, allowing a trans-gradient to be calculated. The core according to the current invention had a trans-gradient that about 44 percent from edge to center. For the core prepared according to the current invention, the pre- and post-cure trans-percentages was also measured to determine the effectiveness of that process. The percentage of polybutadiene converted to the trans-isomer ranged from almost 26 percent at the center to greater than 45 percent at the edge. Two of the cores prepared in accordance with U.S. Pat. Nos. 3,239,228 and 4,692,497 had a zero trans-gradient. A third core prepared in accordance with U.S. Pat. No. 5,697,856 had only a slight trans-gradient, less than 18 percent from edge to center. A fourth core, prepared in accordance with U.S. Pat. No. 5,252,652 had a very large gradient, almost 65 percent from edge to center.

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Example 4

Comparison of a Conventional Dual Core Ball to
Dual Core Ball Prepared According to the
Invention

A dual core golf ball according to the present invention was created having a solid center, an intermediate layer surrounding the solid center, and a multilayer cover disposed concentrically around the intermediate layer. The components and physical characteristics are presented below in Table 5.

TABLE 5

Example 4: Dual Core	
<u>Center Composition</u>	
CARIFLEX BR1220	100
zinc diacrylate	20
dicumyl peroxide	2.5
zinc oxide	39
DTDS	0.75
<u>Center Properties</u>	
% trans Precure	1.5
% trans Postcure	40
load in lbs required (10.8% deflection)	109
<u>Mantle Composition</u>	
CB23	80
zinc diacrylate	38
VAROX 231 XL	0.42
DBDB-60	0.15
zinc oxide	6
polyisoprene	20
<u>Inner Cover Composition and Properties</u>	
Na SURLYN	50
Li SURLYN	50
Shore D hardness	68
thickness	0.03 in
<u>Outer Cover Composition and Properties</u>	
MDI polyurethane	
thickness	0.03 in

A solid center was constructed for the ball of the present invention. The center was created from CARIFLEX BR-1220 polybutadiene as the starting material, the only difference being replacing the VAROX 802-40KE-HP peroxide (conventional technology) with a DTDS cis-to-trans catalyst of the current invention and dicumyl peroxide. This substitution allows a portion of the polybutadiene material to be converted to the trans-configuration during the molding process. The resulting solid center had an outside diameter of approximately 1.15 inches. The polybutadiene reaction product prepared thereby had a trans-isomer content of 40 percent compared to the 1.5 percent trans-isomer of conventional balls. An intermediate layer, having outside diameter of approximately 1.56 inches, was constructed around the solid center to form a core. The outer layer is made of CB23 having a molecular weight of about 360,000 and a Mooney viscosity of about 51.

Examples 5-8

Comparison of Conventional Golf Balls with Those
Prepared According to the Invention

A polybutadiene reaction product was prepared for two conventional prior art compositions (Examples 5-6) as well as one prepared according to the invention (Examples 7-8). The recipes for each composition can be seen in Table 6 below.

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TABLE 6

Reaction Product	Example 5 (phr)	Example 6 (phr)	Example 7 (phr)	Example 8 (phr)
CARIFLEX BR1220	100	100	100	100
zinc oxide	26.6	2.67	26.6	26.6
barium sulfate	—	31	—	—
zinc diacrylate	20	22.3	20	20
dicumyl peroxide	2	—	2	2
VAROX 802 40KE-HP*	—	0.89	—	—
polymeric sulfur	0	0	0.25	0
elemental sulfur	0	0	0	0.25
pre-cure trans-polybutadiene content	1.5%	1.5%	1.5%	1.5%
Golf Ball Core				
post-cure trans-polybutadiene content in reaction product	1.5%	1.5%	12%	12%
Atti Compression	53	23	26	21
COR	n/a ^b	0.72	0.77	0.76

*A di-(2-t-butylisopropylperoxy)-benzene peroxide commercially available from R.T. Vanderbilt of Norwalk, CT.

^bThe core of Example 5 was sufficiently rigid to crack during testing of the coefficient of restitution, indicating an undesirably low COR.

These constituents were mixed and molded, thereby converting a percentage of cis- to a trans-conformation, in a solid sphere sized like the core of a golf ball. Examples 7-8 illustrate the significant conversion of cis-polybutadiene to trans-polybutadiene when a sulfur cis-to-trans catalyst is present according to the invention compared to the lack of conversion in Examples 5-6 when no sulfur catalyst is present. Moreover, Examples 7-8 illustrate the improved coefficient of restitution with no significant change in compression that can be achieved with golf balls including the reaction product according to the invention.

The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball comprising:

a center comprising a material formed from a conversion reaction of polybutadiene having a first amount of trans-isomer, a free radical source, and at least one cis-to-trans catalyst, wherein the material has a molecular weight of greater than about 200,000 and a resilience index of at least about 40; and

a cover layer comprising a polyurethane composition formed from a prepolymer having no greater than 7.5 percent by weight unreacted isocyanate groups.

2. The golf ball of claim 1, wherein the resilience index is greater than about 50.

3. The golf ball of claim 1, wherein the polyurethane composition comprises at least one isocyanate, at least one polyol, and at least one curing agent.

4. The golf ball of claim 3, wherein the isocyanate comprises 4,4'-diphenylmethane diisocyanate, polymeric 4,4'-diphenylmethane diisocyanate, carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, p-phenylene diisocyanate, toluene diisocyanate, isophoronediiisocyanate, p-methylxylene diisocyanate, m-methylxylene diisocyanate, o-methylxylene diisocyanate, or a mixture thereof.

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5. The golf ball of claim 3, wherein the at least one polyol comprises a polyether polyol, hydroxy-terminated polybutadiene, polyester polyol, polycaprolactone polyol, polycarbonate polyol, or mixtures thereof.

6. The golf ball of claim 3, wherein the curing agent comprises a polyamine curing agent, a polyol curing agent, or a mixture thereof.

7. The golf ball of claim 6, wherein the curing agent is a polyamine curing agent.

8. The golf ball of claim 7, wherein the polyamine curing agent comprises 3,5-dimethylthio-2,4-toluenediamine, or an isomer thereof; 3,5-diethyltoluene-2,4-diamine, or an isomer thereof; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene dianiline; phenylenediamine; 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2', 3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); or mixtures thereof.

9. The golf ball of claim 6, wherein the curing agent is a polyol curing agent.

10. The golf ball of claim 9, wherein the polyol curing agent comprises ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β-hydroxyethyl)ether; hydroquinone-di-(β-hydroxyethyl) ether; trimethylol propane, or mixtures thereof.

11. The golf ball of claim 1, wherein the prepolymer has from about 2.5 percent up to 7.5 percent by weight unreacted isocyanate groups.

12. The golf ball of claim 1, wherein the cover layer has a thickness of less than about 0.05 inches.

13. The golf ball of claim 1, wherein the center has a Mooney viscosity from about 40 to about 80.

14. The golf ball of claim 13, wherein the Mooney viscosity from about 45 to about 60.

15. The golf ball of claim 1, wherein the polybutadiene has a vinyl-isomer content of less than about 2 percent by weight.

16. The golf ball of claim 1, wherein the polybutadiene has a cis-isomer content of at least about 95 percent by weight.

17. The golf ball of claim 1, wherein the center has an outer diameter of at least about 1.55 inches.

18. The golf ball of claim 1, wherein the polyurethane is thermoplastic or thermoset.

19. The golf ball of claim 1, wherein the reaction occurs at a temperature sufficient to form a polybutadiene reaction product having a second amount of trans-isomer greater than the first amount of trans-isomer.

20. The golf ball of claim 1, wherein the cis-to-trans catalyst further comprises at least one of an organosulfur compound, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound.

21. The golf ball of claim 20, wherein the organosulfur component comprises at least one of 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide.

22. The golf ball of claim 1, wherein the cis-to-trans catalyst is present in an amount from about 0.1 to 10 parts per hundred of polybutadiene.

23. The golf ball of claim 1, further comprising an intermediate layer between the center and the cover layer,

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wherein the intermediate layer comprises a material formed from a conversion reaction of polybutadiene having a first amount of trans-polybutadiene, a free radical source, and a cis-to-trans catalyst comprising at least one organosulfur component, wherein the intermediate layer has an outer diameter of at least about 1.58 inches, and wherein the center has an outer diameter of less than about 1.55 inches

24. The golf ball of claim 1, wherein the cover comprises an inner cover layer and an outer cover layer, the inner cover layer disposed between the center and the outer cover layer.

25. The golf ball of claim 24, wherein at least one of the inner and outer cover layer has a thickness of less than about 0.05 inches.

26. The golf ball of claim 24, wherein the inner cover layer comprises an ionomer resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer nylon, acrylonitrile butadiene-styrene copolymer, or blends thereof.

27. The golf ball of claim 24, wherein the inner cover has an outer diameter of at least about 1.55 inches.

28. The golf ball of claim 24, wherein the inner cover has an outer diameter of about 1.58 to about 1.64 inches.

29. A golf ball comprising:

a center comprising a material formed from a conversion reaction of polybutadiene having a first amount of trans-isomer, a free radical source, and at least one cis-to-trans catalyst, wherein the material has a molecular weight of greater than about 300,000 and a resilience index of at least about 40;

a outer core layer surrounding the center, the outer core layer having an outer diameter of at least about 1.51 inches;

an inner cover layer surrounding the outer core layer; and an outer cover layer disposed about the inner cover layer, the outer cover layer comprising a polyurethane composition formed from a prepolymer having less than 7.5 percent by weight unreacted isocyanate groups.

30. The golf ball of claim 29, wherein the polyurethane is thermoplastic or thermoset

31. The golf ball of claim 29, wherein the resilience index is greater than about 50.

32. The golf ball of claim 29, wherein the polyurethane composition comprises an isocyanate, at least one polyol, and at least one curing agent

33. The golf ball of claim 32, wherein the isocyanate comprises 4,4'-diphenylmethane diisocyanate, polymeric 4,4'-diphenylmethane diisocyanate, carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, p-phenylene diisocyanate, toluene diisocyanate, isophoronediiisocyanate, p-methylxylene diisocyanate, m-methylxylene diisocyanate, o-methylxylene diisocyanate, or a mixture thereof.

34. The golf ball of claim 32, wherein the at least one polyol comprises a polyether polyol, hydroxy-terminated polybutadiene, polyester polyol, polycaprolactone polyol, polycarbonate polyol, or mixtures thereof.

35. The golf ball of claim 32, wherein the curing agent comprises a polyamine curing agent, a polyol curing agent, or a mixture thereof.

36. The golf ball of claim 35, wherein the curing agent is a polyamine curing agent comprising 3,5-dimethylthio-2,4-tolenediamine, or an isomer thereof; 3,5-diethyltoluene-2,4-diamine, or an and isomer thereof; 4,4'-bis-(sec-

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butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkylidiamino diphenyl methane; p,p'-methylene dianiline; m-phenylenediamine; 4,4'-methylene-bis-(2-chloroaniline); 4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); or mixtures thereof

37. The golf ball of claim 35, wherein the curing agent is a polyol curing agent comprising ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy)benzene; 1,3-bis-[2-(2-hydroxyethoxy)ethoxy]benzene; 1,3-bis-[2-(2-hydroxy)ethoxy]ethoxy]ethoxy benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(hydroxyethyl)ether; hydroquinone-di-(hydroxyethyl)ether; trimethylol propane, or mixtures thereof.

38. The golf ball of claim 29, wherein the prepolymer has from about 2.5 percent up to 7.5 percent by weight unreacted isocyanate groups.

39. The golf ball of claim 29, wherein at least one of the inner and outer cover layers has a thickness of less than about 0.05 inches.

40. The golf ball of claim 29, wherein the center has a Mooney viscosity of from about 40 to about 80.

41. The golf ball of claim 29, wherein the polybutadiene has a vinyl-isomer content of less than about 2 percent by weight.

42. The golf ball of claim 29, wherein the polybutadiene has a cis-isomer content of at least about 95 percent by weight.

43. The golf ball of claim 29, wherein the center has an outer diameter of no greater than about 1.55 inches.

44. The golf ball of claim 29, wherein the reaction occurs at a temperature sufficient to form a polybutadiene reaction product having a second amount of trans-isomer greater than the first amount of trans-isomer.

45. The golf ball of claim 29, wherein the cis-to-trans catalyst further comprises at least one of an organosulfur compound, an inorganic sulfur compound, an aromatic organometallic compound, a metal-organosulfur compound, tellurium, selenium, elemental sulfur, a polymeric sulfur, or an aromatic organic compound.

46. The golf ball of claim 45, wherein the organosulfur component comprises at least one of 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide.

47. The golf ball of claim 29, wherein the cis-to-trans catalyst is present in an amount from about 0.1 to 10 parts per hundred of polybutadiene.

48. The golf ball of claim 29, wherein the inner cover layer comprises an ionomer resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer, nylon, acrylonitrile butadiene-styrene copolymer or blends thereof.

49. The golf ball of claim 29, wherein the inner cover has an outer diameter of at least about 1.55 inches.

50. The golf ball of claim 49, wherein the inner cover has an outer diameter of about 1.58 to about 1.64 inches

* * * * *

EXHIBIT C



US005252652A

United States Patent [19]

Egashira et al.

[11] Patent Number: **5,252,652**[45] Date of Patent: **Oct. 12, 1993**[54] **SOLID GOLF BALL**

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A63B 37/00

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524/382; 524/908; 273/218

[58] Field of Search 524/908, 289, 382, 392

[56] References Cited

U.S. PATENT DOCUMENTS

2,378,519 6/1945 Vincent 524/392
2,467,789 4/1949 Verbanc et al. 524/382

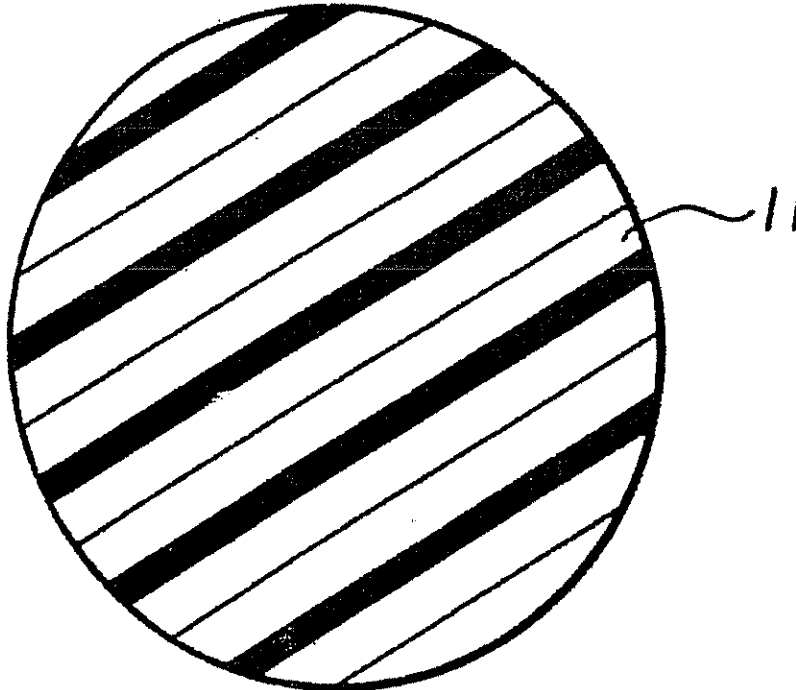
2,543,845 3/1951 Fryling 524/392
3,175,992 3/1965 Anderson, Jr. 524/392
3,804,421 4/1974 Alex et al. 293/218
3,923,719 12/1975 Gattuso 524/392
4,076,255 2/1978 Moore et al. 273/218
4,129,538 12/1978 Kaplan et al. 524/392
4,398,000 8/1983 Kataoka et al. 523/206
4,556,220 12/1985 Tomina et al. 524/908
4,595,721 6/1986 Devaux et al. 524/392
4,683,257 7/1987 Kakiuchi et al. 524/908
4,735,980 4/1988 Sturm et al. 524/392
4,770,422 9/1988 Isaac 524/708

Primary Examiner—Kriellion S. Morgan
Attorney, Agent, or Firm—Sughrue, Mion, Zinn,
Macpeak & Seas

[57] **ABSTRACT**

One-piece and multi-layered golf balls are improved in flying performance by forming the one-piece ball entirely or multi-layered golf ball core from a rubber composition comprising a base rubber, an unsaturated carboxylic acid metal salt, and an organic sulfur compound and/or a metal salt thereof.

13 Claims, 1 Drawing Sheet



U.S. Patent

Oct. 12, 1993

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FIG. 1

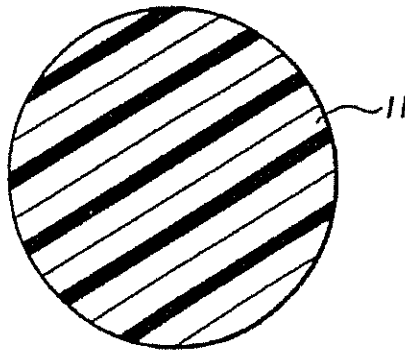
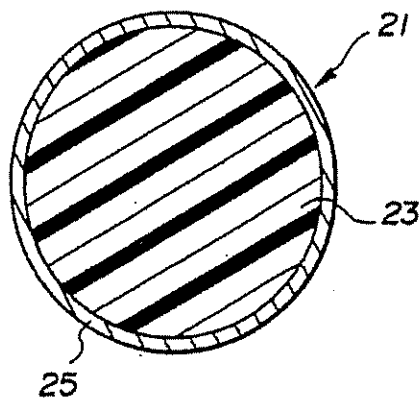


FIG. 2



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about 0.1 to about 0.5 parts by weight per 100 parts by weight of the base rubber.

The rubber composition of the invention may further contain a co-crosslinking initiator. Preferred examples of the co-crosslinking initiator include organic peroxides, such as dicumyl peroxide, t-butylperoxybenzoate, di-t-butylperoxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethyl-cyclohexane, n-butyl-4,4-bis(t-butylperoxy)valerate, 2,2-bis(t-butylperoxy-isopropyl)benzene, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexene, with the dicumyl peroxide being most preferred. The initiator may be blended in amounts of about 0.5 to about 3 parts by weight, preferably about 1 to about 2.5 parts by weight per 100 parts by weight of the base rubber.

Also employable is a filler. Preferred examples of the filler include metal oxides such as zinc oxide and magnesium oxide. It may be blended in amounts of about 10 to about 80 parts by weight per 100 parts by weight of the base rubber. If desired, the rubber composition can additionally contain a plasticizer, an antioxidant, and any other additives which are generally employed in the preparation of one-piece balls or cores of multi-layered balls. Their amounts may be determined without undue experimentation.

The solid golf ball of the invention may be prepared by molding the above-formulated rubber composition as formulated above into a desired spherical shape, that is, a ball in the case of a one-piece ball or into a core in the case of a multi-layered ball and vulcanizing the rubber by heating. The manufacture may be in accord with conventional method and conditions.

When multi-layered golf balls such as two-piece balls are manufactured, the core is coated with a cover. The cover material used herein may be selected from commonly used cover materials, for example, ionomers such as Surlyn®, polyesters, and nylons. The cover usually has a thickness of 0.5 to 2.5 mm.

The core may be enclosed in the cover directly or through an intermediate layer.

The present invention may be applied to any type of golf ball including small balls having a diameter of at least 41.15 mm and a weight of up to 45.92 g, and large balls having a diameter of at least 42.67 mm and a weight of up to 45.92 g.

The distribution and total number of dimples are not critical although 300 to 550 dimples, preferably 350 to 540 dimples are generally formed on a ball. Preferred dimple arrangements are regular icosahedral, regular dodecahedral, and regular octahedral arrangements. The dimples is preferably distributed uniformly on the ball surface in such an arrangement.

The solid golf balls of the invention are of the above-mentioned construction and exhibit excellent flying performance.

EXAMPLE

Examples of the invention are given below together with comparative examples by way of illustration and not by way of limitation.

EXAMPLES 1-6

Solid cores for two-piece golf balls were prepared and compared with conventional two-piece golf ball cores.

Six rubber compositions were prepared by mixing the ingredients shown in Table 1. A two-piece golf ball-forming solid core having a diameter of 38.0 mm was prepared by molding each of the compositions in a mold

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followed by vulcanization at 155° C. for 20 minutes. The cores were examined by a hitting test according to the USGA standard. Using a hitting machine of the flywheel type, the cores were hit at a head speed of 38 m/sec. to measure the initial velocity (in m/sec.). The results are shown in Table 1.

TABLE 1

	Core No.					
	1	2	3	4*	5*	6*
<u>Ingredients (pbw)</u>						
Poly(cis-1,4-butadiene)	100	90	80	100	90	80
Poly(cis-isoprene)	0	10	20	0	10	20
Zinc acrylate	32	32	32	32	32	32
Zinc oxide	21	21	21	21	21	21
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2
Dicumyl peroxide	1.5	1.5	1.5	1.5	1.5	1.5
Pentachlorothiophenol zinc salt	0.2	0.2	0.2	0	0	0
Initial velocity, m/sec.	73.32	73.11	72.80	72.95	72.67	72.30

*outside the scope of the invention

As seen from Table 1, the performance, that is, initial velocity upon hitting of the core is improved by blending zinc salt of pentachlorothiophenol which is a metal salt of an organic sulfur compound in a rubber composition.

Examples 7 and 8

Two rubber compositions were prepared by blending the ingredients shown in Table 2. Two-piece golf ball solid cores having a diameter of 38 mm were prepared by molding the composition in a mold and vulcanizing at 155° C. for 20 minutes. An ionomer resin composition was applied to the cores to form a cover thereon. There were obtained two-piece golf balls having a diameter of 42.7 mm.

The balls were measured for weight, hardness and initial velocity. The hardness of the balls was measured as a deflection (in mm) under a load of 100 kg. The initial velocity (in m/sec.) of the balls was measured by a hitting test according to the USGA standard in which the balls were hit at a head speed of 38 m/sec. using a hitting machine of the flywheel type. The results are shown in Table 2.

TABLE 2

	Example	
	7	8*
<u>Core composition (pbw)</u>		
Poly(cis-1,4-butadiene) rubber	100	100
Zinc acrylate	32	32
Zinc oxide	21	21
Antioxidant	0.2	0.2
Dicumyl peroxide	1.5	1.5
Pentachlorothiophenol zinc salt	0.2	—
<u>Ball properties</u>		
Weight, g	45.3	45.3
Hardness	2.30	2.32
Initial velocity, m/sec.	73.37	72.84

*outside the scope of the invention

As seen from Table 1, the golf balls of the invention are improved in initial velocity upon hitting and hence, in flying performance.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the

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appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. A solid golf ball, having an improved rebound property and initial velocity, comprising a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber, about 25 to about 40 parts by weight of a zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms, about 0.05 to about 2 parts by weight of a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2-benzamidothiophenol, thiobenzoic acid, and zinc salts thereof, and about 0.5 to about 3 parts by weight of an organic peroxide.

2. The solid golf ball of claim 1, wherein said solid golf ball is a one-piece golf ball which is formed of said rubber composition.

3. The solid golf ball of claim 1, wherein said solid golf ball core and a cover enclosing the core, and said core is formed of said rubber composition.

4. The solid golf ball of claim 3, wherein said solid golf ball is a two-piece ball, and said core is directly enclosed in the cover.

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5. The solid golf ball of claim 3, wherein said solid golf ball further comprises an intermediate layer between the core and the cover.

6. The solid golf ball of claim 1, wherein said base rubber is a polybutadiene rubber.

7. The solid golf ball of claim 6, wherein said polybutadiene rubber is a poly(1,4-butadiene) rubber containing at least 40 mol % of cis-1,4 bond.

8. The solid golf ball of claim 7, wherein said poly(1,4-butadiene) rubber contains at least 80 to 100 mol % of cis-1,4 bond.

9. The solid golf ball of claim 7, wherein said base rubber comprises at least 80% by weight of said poly(1,4-butadiene) rubber.

10. The solid golf ball of claim 9, wherein said poly(1,4-butadiene) rubber is blended with a natural rubber, a polyisoprene rubber or a styrene-butadiene rubber.

11. The solid golf ball of claim 1, wherein said sulfur compound is blended in an amount of from about 0.1 to about 0.5 parts by weight.

12. The solid golf ball of claim 1, wherein said organic peroxide is selected from the group consisting of dicumyl peroxide, t-butylperoxybenzoate, di-t-butylperoxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, n-butyl-4,4-bis(t-butylperoxy)valerate, 2,2'-bis(t-butylperoxyisopropyl)benzene, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexene.

13. The solid golf ball of claim 1, wherein said rubber composition further comprises a filler.

* * * * *

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EXHIBIT D

**THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY**

EXHIBIT E

**THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY**

EXHIBIT F

IN UNITED STATES DISTRICT COURT
DISTRICT OF DELAWARE

BRIDGESTONE SPORTS CO., LTD.,
AND BRIDGESTONE GOLF, INC.,

Plaintiffs,

v.

ACUSHNET COMPANY,

Defendant.

C.A. No. 05-132(JJF)

DEMAND FOR JURY TRIAL

PLAINTIFFS' RESPONSES TO DEFENDANT'S FIRST SET OF INTERROGATORIES

Pursuant to Rule 33 of the Federal Rules of Civil Procedure, Plaintiffs Bridgestone Sports Co., Ltd., and Bridgestone Golf, Inc., (individually or collectively "Bridgestone") hereby respond to Defendant's First Set Of Interrogatories To Plaintiff dated June 10, 2005.

GENERAL OBJECTIONS

The following general objections are made to each and every interrogatory, irrespective of whether they are stated specifically in response thereto:

1. The following responses are based upon information presently available to and located by Bridgestone and its attorneys. Bridgestone has not completed its investigation of the facts relating to this action, and has not completed discovery in this action. Bridgestone's responses are based upon (1) a reasonable search, given the time allotted to Bridgestone to respond to the interrogatories, and (2) inquiries of Bridgestone employees and/or representatives who could reasonably be expected to possess responsive information. The subject matter of these requests is under continuing investigation. Bridgestone's responses are without prejudice to its rights to identify and to use additional information revealed in subsequent investigations and discovery.

9. At least claims 1-6, 10-17, and 21-23 of the '791 patent are infringed by at least one or more of the Titleist® Pro V1™ and Titleist® Pro V1x™ golf balls, and all other golf balls made or sold by Acushnet under a different brand and being substantially identical to any of the foregoing golf balls.

10. At least claims 2, 3 and 5-14 of the '125 patent are infringed by at least one or more of the Titleist® Pro V1™ and Titleist® Pro V1x™ golf balls, and all other golf balls made or sold by Acushnet under a different brand and being substantially identical to any of the foregoing golf balls.

Bridgestone reserves the right to later amend or supplement its contentions after further investigation and discovery and after the Court construes the claims.

INTERROGATORY NO. 2

For each claim that is alleged to be infringed by Acushnet in your RESPONSE TO INTERROGATORY NO. 1, provide a claim chart that describes in detail on an element-by-element basis how you contend each product identified infringes each claim, specifying whether such infringement is alleged to be literal and/or under the doctrine of equivalents.

RESPONSE TO INTERROGATORY NO. 2

In addition to the General Objections, Bridgestone objects to the interrogatory as being a multiple and compound request constituting more than one interrogatory. Bridgestone also objects to the interrogatory as being premature at this early stage of discovery, particularly since Bridgestone does not have the benefit of Acushnet's discovery, the Court has not construed the claims of the Bridgestone Patents, and the interrogatory calls for expert opinion and expert discovery. In addition, Bridgestone objects to this interrogatory as premature to the extent it seeks Bridgestone's contentions regarding claim construction. Subject to and without waiving the general and specific objections, and upon information and belief, Bridgestone responds with the claim charts set forth in Appendices A-J hereto.

Infringement is literal and under the doctrine of equivalents. In the event that any element of a claim is later found not to be literally present in an accused product, Bridgestone maintains that the accused product includes an equivalent of that element and infringes the claim under the doctrine of equivalents.

Bridgestone reserves the right to later amend or supplement its contentions after further investigation and discovery and after the Court construes the claims.

INTERROGATORY NO. 3

Identify on a claim-by-claim basis all facts that support your contention that Acushnet has engaged in contributory infringement and/or inducement of infringement of the Bridgestone Patents.

RESPONSE TO INTERROGATORY NO. 3

In addition to the General Objections, Bridgestone objects to the interrogatory as being premature at this early stage of discovery; particularly since Bridgestone does not have the benefit of Acushnet's discovery and the Court has not construed the claims of the Bridgestone Patents. In addition, Bridgestone objects to this interrogatory as premature to the extent it seeks Bridgestone's contentions regarding claim construction. Subject to and without waiving the general and specific objections, Bridgestone incorporates its responses to Interrogatories 1 and 2 herein and further responds that Acushnet is actively inducing infringement and contributing to the infringement of the Bridgestone Patents by knowingly manufacturing, offering to sell, selling, advertising, marketing, promoting and engaging in other supporting activities to induce others to sell and use the infringing products.

Bridgestone reserves the right to later amend or supplement its contentions after further investigation, discovery and after the Court construes the claims.

APPENDIX A: CLAIM CHART FOR THE '652 PATENT

Page A-1

APPENDIX A: CLAIM CHART FOR THE '652 PATENT (Pro V1)

The '652 Patent	Pro V1 (2003-present)
CLAIM 1	
1. A solid golf ball, having an improved rebound property and initial velocity, comprising;	The Pro V1 is a solid golf ball having an improved rebound property and initial velocity.
a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber,	The Pro V1 has a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber.
about 25 to about 40 parts by weight of a zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms,	The Pro V1 has a rubber composition containing zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms in an amount within the scope of the claimed range.
about 0.05 to about 2 parts by weight of a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof, and	The Pro V1 has a rubber composition containing a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof in an amount within the scope of the claimed range.
about 0.5 to about 3 parts by weight of an organic peroxide.	The Pro V1 has a rubber composition containing an organic peroxide within the scope of the claimed range.
CLAIM 3	
3. The solid golf ball of claim 1, wherein said solid golf ball core and a cover enclosing the core, and said core is formed of said rubber composition.	The Pro V1 comprises a core and a cover, wherein the core comprises the rubber composition described above.
CLAIM 5	

APPENDIX A: CLAIM CHART FOR THE '652 PATENT

Page A-4

APPENDIX A: CLAIM CHART FOR THE '652 PATENT (Pro V1x)

The '652 Patent	Pro V1x (2003-present)
CLAIM 1	
1. A solid golf ball, having an improved rebound property and initial velocity, comprising;	The Pro V1x is a solid golf ball having an improved rebound property and initial velocity.
a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber,	The Pro V1x has a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber.
about 25 to about 40 parts by weight of a zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms,	The Pro V1 has a rubber composition containing zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms in an amount within the scope of the claimed range.
about 0.05 to about 2 parts by weight of a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof, and	The Pro V1x has a rubber composition containing a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof in an amount within the scope of the claimed range.
about 0.5 to about 3 parts by weight of an organic peroxide.	The Pro V1x has a rubber composition containing an organic peroxide within the scope of the claimed range
CLAIM 3	
3. The solid gold ball of claim 1, wherein said solid golf ball core and a cover enclosing the core, and said core is formed of said rubber composition.	The Pro V1x comprises a core and a cover, wherein the core comprises the rubber composition described above.
CLAIM 5	

APPENDIX A: CLAIM CHART FOR THE '652 PATENT

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APPENDIX A: CLAIM CHART FOR THE '652 PATENT (NXT Tour)

The '652 Patent	NXT Tour (2003-present)
CLAIM 1	
1. A solid golf ball, having an improved rebound property and initial velocity, comprising;	The NXT Tour is a solid golf ball having an improved rebound property and initial velocity.
a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber,	The NXT Tour has a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber.
about 25 to about 40 parts by weight of a zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms,	The NXT Tour has a rubber composition containing zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms in an amount within the scope of the claimed range.
about 0.05 to about 2 parts by weight of a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof, and	The NXT Tour has a rubber composition containing a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof in an amount within the scope of the claimed range.
about 0.5 to about 3 parts by weight of an organic peroxide.	The NXT Tour has a rubber composition containing an organic peroxide within the scope of the claimed range.
CLAIM 3	
3. The solid golf ball of claim 1, wherein said solid golf ball core and a cover enclosing the core, and said core is formed of said rubber composition.	The NXT Tour comprises a core and a cover, wherein the core comprises the rubber composition described above.
CLAIM 4	

APPENDIX A: CLAIM CHART FOR THE '652 PATENT

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APPENDIX A: CLAIM CHART FOR THE '652 PATENT (NXT)

The '652 Patent	NXT (2003-present)
CLAIM 1	
1. A solid golf ball, having an improved rebound property and initial velocity, comprising;	The NXT is a solid golf ball having an improved rebound property and initial velocity.
a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber,	The NXT has a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber.
about 25 to about 40 parts by weight of a zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms,	The NXT has a rubber composition containing zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms in an amount within the scope of the claimed range.
about 0.05 to about 2 parts by weight of a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof, and	The NXT has a rubber composition containing a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof in an amount within the scope of the claimed range.
about 0.5 to about 3 parts by weight of an organic peroxide.	The NXT has a rubber composition containing an organic peroxide within the scope of the claimed range.
CLAIM 3	
3. The solid gold ball of claim 1, wherein said solid golf ball core and a cover enclosing the core, and said core is formed of said rubber composition.	The NXT comprises a core and a cover, wherein the core comprises the rubber composition described above.
CLAIM 4	

APPENDIX A: CLAIM CHART FOR THE '652 PATENT

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APPENDIX A: CLAIM CHART FOR THE '652 PATENT (DT SoLo)

The '652 Patent	DT SoLo (2003-present)
CLAIM 1	
1. A solid golf ball, having an improved rebound property and initial velocity, comprising;	The DT SoLo is solid golf ball having an improved rebound property and initial velocity.
a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber,	The DT SoLo has a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber.
about 25 to about 40 parts by weight of a zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms,	The DT SoLo has a rubber composition containing a zinc magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms in an amount within the scope of the claimed range.
about 0.05 to about 2 parts by weight of a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof, and	The DT SoLo has a rubber composition containing a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof in an amount within the scope of the claimed range.
about 0.5 to about 3 parts by weight of an organic peroxide.	The DT SoLo has a rubber composition containing an organic peroxide within the scope of the claimed range.
CLAIM 3	
3. The solid golf ball of claim 1, wherein said solid golf ball core and a cover enclosing the core, and said core is formed of said rubber composition.	The DT SoLo comprises a core and a cover, wherein the core comprises the rubber composition described above.
CLAIM 4	

APPENDIX A: CLAIM CHART FOR THE '652 PATENT

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APPENDIX A: CLAIM CHART FOR THE '652 PATENT (Pinnacle Exception)

The '652 Patent	Pinnacle Exception
CLAIM 1	
1. A solid golf ball, having an improved rebound property and initial velocity, comprising;	The Pinnacle Exception is a two-piece solid golf ball having an improved rebound property and initial velocity.
a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber,	The Pinnacle Exception has a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber.
about 25 to about 40 parts by weight of a zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms,	The Pinnacle Exception has a rubber composition containing zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms in an amount within the scope of the claimed range.
about 0.05 to about 2 parts by weight of a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof, and	The Pinnacle Exception has a rubber composition containing a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2 benzamidothiophenol, thiobenzoic acid, and zinc salts thereof in an amount within the scope of the claimed range.
about 0.5 to about 3 parts by weight of an organic peroxide.	The Pinnacle Exception has a rubber composition containing an organic peroxide within the scope of the claimed range.
CLAIM 3	
3. The solid gold ball of claim 1, wherein said solid golf ball core and a cover enclosing the core, and said core is formed of said rubber composition.	The Pinnacle Exception comprises a core and a cover, wherein the core comprises the rubber composition described above.
CLAIM 4	

EXHIBIT G

**THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY**

EXHIBIT H



US006634961B2

(12) **United States Patent**
Higuchi et al.

(10) Patent No.: **US 6,634,961 B2**
(45) Date of Patent: ***Oct. 21, 2003**

(54) **MULTI-PIECE SOLID GOLF BALL**

(75) Inventors: **Hiroshi Higuchi, Chichibu (JP);**
Atsushi Nanba, Chichibu (JP)

(73) Assignee: **Bridgestone Sports Co., Ltd., Tokyo**
(JP)

(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

This patent is subject to a terminal dis-
claimer.

(21) Appl. No.: **10/156,950**

(22) Filed: **May 30, 2002**

(65) **Prior Publication Data**

US 2003/0017888 A1 Jan. 23, 2003

(30) **Foreign Application Priority Data**

May 30, 2001 (JP) 2001-163238

(51) Int. Cl.⁷ **A63B 37/06**

(52) U.S. Cl. **473/357; 524/432**

(58) Field of Search **473/357, 356,**
473/359, 372, 374, 371, 373; 524/194,
908, 432, 526, 534

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,683,257 A * 7/1987 Kakiuchi et al. 473/372
4,929,678 A * 5/1990 Hamada et al. 525/193
4,955,613 A * 9/1990 Gendreau et al. 260/998.14
5,252,652 A * 10/1993 Egashira et al. 473/372

5,733,205 A * 3/1998 Higuchi et al. 473/373
6,045,460 A * 4/2000 Hayashi et al. 473/376
6,194,505 B1 * 2/2001 Sone et al. 473/371
6,315,679 B1 * 11/2001 Sano 473/357

FOREIGN PATENT DOCUMENTS

EP 0 920 886 A2 6/1999
GB 2 324 740 A 11/1998

OTHER PUBLICATIONS

M. R. Farrally, A. J. Cochran, "Science and Golf III", 1999,
Human Kinetics, pp. 410, 412, 413.*
British Search Report, Oct. 17, 2002.

* cited by examiner

Primary Examiner—Paul T. Sewell

Assistant Examiner—Tom P Duong

(74) Attorney, Agent, or Firm—Sughrue Mion, PLLC

(57) **ABSTRACT**

In a multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, the solid core is molded from a rubber composition comprising a base rubber composed of (a) 20–100 wt % of a polybutadiene having a high cis-1,4 content, a minimal 1,2 vinyl content and a viscosity η of up to 600 mPa·s at 25° C as a 5 wt % toluene solution, and satisfying a certain relationship between Mooney viscosity and polydispersity index in combination with (b) 0–80 wt % of another diene rubber, (c) an unsaturated carboxylic acid, (d) an organosulfur compound, (e) an inorganic filler, and (f) an organic peroxide; and the outer cover layer has a lower Shore D hardness than the inner cover layer. This combination of features gives the ball a good, soft feel upon impact and an excellent spin performance that provides increased distance.

9 Claims, No Drawings

US 6,634,961 B2

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MULTI-PIECE SOLID GOLF BALL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a multi-piece solid golf ball which has been imparted with a good, soft feel upon impact and an excellent spin performance that makes it possible to achieve an increased distance.

2. Prior Art

Various improvements are being made in formulating the polybutadiene used as the base rubber in golf balls so as to confer the balls with outstanding rebound characteristics.

For example, JP-A 62-89750 describes rubber compositions for use as the base rubber in solid golf balls, which compositions are arrived at by blending a polybutadiene having a Mooney viscosity of 70 to 100 and synthesized using a nickel or cobalt catalyst with another polybutadiene having a Mooney viscosity of 30 to 90 and synthesized using a lanthanide catalyst or polybutadiene having a Mooney viscosity of 20 to 50 and synthesized using a nickel or cobalt catalyst.

However, further improvements in the materials are required in the above art to achieve golf balls endowed with a good, soft feel upon impact and an excellent spin performance that helps increase the distance the ball travels when played.

JP-A 2-268778 describes golf balls molded using a blend composed of a polybutadiene having a Mooney viscosity of less than 50 and synthesized using a Group VIII catalyst in combination with a polybutadiene having a Mooney viscosity of less than 50 and synthesized with a lanthanide catalyst. However, golf balls with a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball cannot be obtained in this way.

The existing art also teaches multi-piece solid golf balls in which an intermediate layer is molded of a low-Mooney viscosity polybutadiene (JP-A 11-70187), solid golf balls molded from rubber compositions comprising a polybutadiene having a Mooney viscosity of 50 to 69 and synthesized using a nickel or cobalt catalyst in combination with a polybutadiene having a Mooney viscosity of 20 to 90 and synthesized using a lanthanide catalyst (JP-A 11-319148), solid golf balls molded from compositions based on a rubber having a 1,2 vinyl content of at most 2.0% and a weight-average molecular weight to number-average molecular weight ratio M_w/M_n of not more than 3.5 (JP-A 11-164912), golf balls molded from rubber compositions containing a high Mooney viscosity polybutadiene (JP-A 63-275356), and golf balls molded from rubber compositions comprising polybutadiene having a high number-average molecular weight in admixture with polybutadiene having a low number-average molecular weight (JP-A 3-151985). However, none of these prior-art golf balls truly have a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball.

Golf balls having a cover composed of a relatively hard inner layer and a relatively soft outer layer have already been disclosed in JP-A 6-218078, JP-A 6-343718, JP-A 7-24085, JP-A 9-239068, JP-A 10-151226, JP-A 10-201880, JP-A 11-104273, JP-A 11-104271, and Japanese Patent Applications No. 2000-274807 and 2000-274843. However, further improvements in distance are desired for the golf balls described in all of these specifications.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide multi-piece solid golf balls which are endowed with a good,

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soft feel when hit with a golf club and an excellent spin performance that helps increase the distance traveled by the ball when played.

The inventor has discovered that golf balls having a solid core, an inner cover layer over the cover, and an outer cover layer over the inner cover layer, wherein the solid core is made of a rubber composition formulated from a particular type of base rubber combined in specific proportions with certain other materials, and the outer cover layer is softer than the inner cover layer, exhibit a good synergy from optimization of the solid core materials and an appropriate distribution of hardness between the inner and outer cover layers. Multi-piece solid golf balls thus constituted have a good, soft feel when hit with a golf club and an excellent spin performance that enables the ball to travel further when played.

Accordingly, the invention provides a multi-piece solid golf ball having a solid core, an inner cover layer enclosing the core, and an outer cover layer enclosing the inner cover layer. The solid core is molded from a rubber composition comprising 100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity η at 25° C as a 5 wt % solution in toluene of up to 600 mPa·s, and satisfying the relationship: $10B + 5 \leq A \leq 10B + 60$, wherein A is the Mooney viscosity ($ML_{1+4}(100^\circ \text{C})$) of the polybutadiene and B is the ratio M_w/M_n between the weight-average molecular weight M_w and the number-average molecular weight M_n of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a). The rubber composition includes also (c) 10 to 60 parts by weight of an unsaturated carboxylic acid and/or a metal salt thereof, (d) 0.1 to 5 parts by weight of an organosulfur compound, (e) 5 to 80 parts by weight of an inorganic filler, and (f) 0.1 to 5 parts by weight of an organic peroxide. The outer cover layer has a lower Shore D hardness than the inner cover layer.

The polybutadiene (a) is typically synthesized using a rare-earth catalyst.

Preferably, the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity ($ML_{1+4}(100^\circ \text{C})$) of not more than 55, and satisfies the relationship $\eta \leq 20A - 550$, wherein A is the Mooney viscosity ($ML_{1+4}(100^\circ \text{C})$) of the second polybutadiene and η is the viscosity, in mPa·s, of the second polybutadiene at 25° C as a 5 wt % solution in toluene. The second polybutadiene in component (b) is typically synthesized using a Group VIII catalyst.

In the multi-piece solid golf ball of the invention, it is generally advantageous for the inner cover layer to have a Shore D hardness of 50 to 80 and the outer cover layer to have a Shore D hardness of 35 to 60.

DETAILED DESCRIPTION OF THE INVENTION

The golf ball of the invention includes a solid core made of a rubber composition in which the base rubber is at least partly polybutadiene. It is critical that the base rubber contain as component (a) a specific amount of a polybutadiene in which the cis-1,4 and 1,2 vinyl contents, the viscosity η at 25° C as a 5 wt % solution in toluene, and the relationship between the Mooney viscosity and the polydispersity index M_w/M_n have each been optimized.

That is, the polybutadiene (a) has a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least

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90%, and most preferably at least 95%; and has a 1,2 vinyl content of at most 2%, preferably at most 1.7%, more preferably at most 1.5%, and most preferably at most 1.3%. Outside of the above ranges, the resilience declines

The polybutadiene (a) must also have a viscosity η at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s. "Viscosity η at 25° C. as a 5 wt % solution in toluene" refers herein to the value in mPa·s units obtained by dissolving 2.28 g of the polybutadiene to be measured in 50 ml of toluene and carrying out measurement with a specified viscometer at 25° C. using a standard solution for the viscometer (JIS Z8809).

The polybutadiene (a) has a viscosity η at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s, preferably not more than 550 mPa·s, more preferably not more than 500 mPa·s, even more preferably not more than 450 mPa·s, and most preferably not more than 400 mPa·s. Too high a viscosity η lowers the workability of the rubber composition. It is recommended that the viscosity η be at least 50 mPa·s, preferably at least 100 mPa·s, more preferably at least 150 mPa·s, and most preferably at least 200 mPa·s. Too low a viscosity η may lower the resilience.

In addition, the polybutadiene (a) must satisfy the relationship:

$$10B+5 \leq A \leq 10B+60,$$

wherein A is the Mooney viscosity (ML_{1+4} (100° C.)) of the polybutadiene and B is the ratio M_w/M_n between the weight-average molecular weight M_w and the number-average molecular weight M_n of the polybutadiene. A is preferably at least $10B+7$, more preferably at least $10B+8$ and most preferably at least $10B+9$, but preferably not more than $10B+55$, more preferably not more than $10B+50$, and most preferably not more than $10B+45$. If A is too low, the resilience declines. On the other hand, if A is too high, the workability of the rubber composition worsens.

It is recommended that the polybutadiene (a) have a Mooney viscosity (ML_{1+4} (100° C.)) of at least 20, preferably at least 30, more preferably at least 40, and most preferably at least 50, but not more than 80, preferably not more than 70, more preferably not more than 65, and most preferably not more than 60.

The term "Mooney viscosity" used herein refers in each case to an industrial index of viscosity as measured with a Mooney viscometer, which is a type of rotary plastometer (see JIS K6300). This value is represented by the symbol ML_{1+4} (100° C.), wherein "M" stands for Mooney viscosity, "L" stands for large rotor (L-type), "1+4" stands for a pre-heating time of 1 minute and a rotor rotation time of 4 minutes, and "100° C." indicates that measurement was carried out at a temperature of 100° C.

It is desirable for the polybutadiene (a) to be synthesized using a rare-earth catalyst. A known rare-earth catalyst may be used for this purpose.

Examples of suitable catalysts include lanthanide series rare-earth compounds, organoaluminum compounds, alumoxane, halogen-bearing compounds, optionally in combination with Lewis bases.

Examples of suitable lanthanide series rare-earth compounds include halides, carboxylates, alcoholates, thioalcoholates and amides of atomic number 57 to 71 metals.

Organoaluminum compounds that may be used include those of the formula $AlR^1R^2R^3$ (wherein R^1 , R^2 and R^3 are

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each independently a hydrogen or a hydrocarbon residue of 1 to 8 carbons).

Preferred alumoxanes include compounds of the structures shown in formulas (I) and (II) below. The alumoxane association complexes described in *Fine Chemical* 23, No. 9, 5 (1994), *J. Am. Chem. Soc.* 115, 4971 (1993), and *J. Am. Chem. Soc.* 117, 6465 (1995) are also acceptable.



In the above formulas, R^4 is a hydrocarbon group having 1 to 20 carbon atoms, and n is 2 or a larger integer.

Examples of halogen-bearing compounds that may be used include aluminum halides of the formula AlX_nR_{3-n} (wherein X is a halogen; R is a hydrocarbon residue of 1 to 20 carbons, such as an alkyl, aryl or aralkyl; and n is 1, 1.5, 2 or 3); strontium halides such as Me_2SrCl , Me_2SrCl_2 , $MeSrHCl_2$ and $MeSrCl_3$ (wherein "Me" stands for methyl); and other metal halides such as silicon tetrachloride, tin tetrachloride and titanium tetrachloride.

The Lewis base may be used to form a complex with the lanthanide series rare-earth compound. Illustrative examples include acetylacetone and ketone alcohols.

In the practice of the invention, the use of a neodymium catalyst composed in part of a neodymium compound as the lanthanide series rare-earth compound is advantageous because it enables a polybutadiene rubber having a high cis-1,4 content and a low 1,2 vinyl content to be obtained at an excellent polymerization activity. Preferred examples of such rare-earth catalysts include those mentioned in JP-A 11-35633.

The polymerization of butadiene in the presence of a rare-earth catalyst may be carried out by bulk polymerization or vapor phase polymerization, either with or without the use of solvent, and at a polymerization temperature in a range of generally -30° C. to +150° C., and preferably 10° C. to 100° C.

It is also possible for the polybutadiene (a) to be obtained by polymerization using the above-described rare-earth catalyst, followed by the reaction of an end group modifier with active end groups on the polymer.

Any known end group modifier may be used. Examples include compounds of types (1) to (6) described below:

(1) halogenated organometallic compounds, halogenated metallic compounds and organometallic compounds of the general formulas $R^5_nM'X_{4-n}$, $M'X_4$, $M'X_3$, $R^5_nM'(-R^6-COOR^7)_{4-n}$ or $R^5_nM'(-R^6-COR^7)_{4-n}$ (wherein R^5 and R^6 are each independently a hydrocarbon group of 1 to 20 carbons; R^7 is a hydrocarbon group of 1 to 20 carbons which may contain a carbonyl or ester moiety as a side chain; M' is a tin atom, silicon atom, germanium atom or phosphorus atom; X is a halogen atom; and n is an integer from 0 to 3);

(2) heterocumulene compounds containing on the molecule a $Y=C=Z$ linkage (wherein Y is a carbon atom, oxygen atom, nitrogen atom or sulfur atom; and Z is an oxygen atom, nitrogen atom or sulfur atom);

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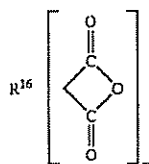
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- (3) three-membered heterocyclic compounds containing on the molecule the following bonds



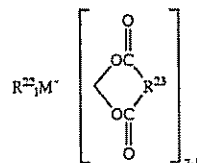
(wherein Y is an oxygen atom, a nitrogen atom or a sulfur atom);

- (4) halogenated isocyanate compounds;
 (5) carboxylic acids, acid halides, ester compounds, carbonate compounds or acid anhydrides of the formulas $R^8-(COOH)_m$, $R^9(COX)_m$, $R^{10}-(COOR^{11})_m$, $R^{12}-OCCO-R^{13}$, $R^{14}-(COOCO-R^{15})_m$ or the following formula



(wherein R^8 to R^{16} are each independently a hydrocarbon group of 1 to 50 carbons; X is a halogen atom; and m is an integer from 1 to 5); and

- (6) carboxylic acid metal salts of the formula $R^{17}_nM^+(OCOR^{18})_{4-n}$, $R^{19}_nM^+(OCO-R^{20}-COOR^{21})_{4-n}$ or the following formula



(wherein R^{17} to R^{23} are each independently a hydrocarbon group of 1 to 20 carbons, M⁺ is a tin atom, a silicon atom or a germanium atom; and n is an integer from 0 to 3).

Illustrative examples of the end group modifiers of types (1) to (6) above and methods for their reaction are described in, for instance, JP-A 11-35633 and JP-A 7-268132.

In the practice of the invention, component (a) is included in the base rubber in an amount of at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, and most preferably at least 35 wt %. The upper limit is 100 wt %, preferably not more than 90 wt %, more preferably not more than 80 wt %, and most preferably not more than 70 wt %.

In addition to component (a), the base rubber may include also a diene rubber (b) insofar as the objects of the invention are attainable. Specific examples of the diene rubbers (b) include polybutadiene rubber, styrene-butadiene rubber (SBR), natural rubber, polyisoprene rubber, and ethylene-propylene-diene rubber (EPDM). Any one or combination of two or more thereof may be used.

The diene rubber (b) is included together with component (a) in the base rubber in an amount of at least 0 wt %, preferably at least 10 wt %, more preferably at least 20 wt %, and most preferably at least 30 wt %, but not more than 80 wt %, preferably not more than 75 wt %, more preferably not more than 70 wt %, and most preferably not more than 65 wt %.

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In the practice of the invention, it is preferable for component (b) to include a polybutadiene rubber, and especially one for which the cis-1,4 and 1,2 vinyl contents, the Mooney viscosity, and the relationship between the Mooney viscosity and η have each been optimized. The polybutadiene serving as component (b) is referred to as "second polybutadiene" in order to distinguish it from the polybutadiene serving as component (a).

It is recommended that the second polybutadiene in component (b) have a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least 90%, and most preferably at least 95%, and that it have a 1,2 vinyl content of at most 5%, preferably at most 4.5%, more preferably at most 4.0%, and most preferably at most 3.5%.

It is recommended that the second polybutadiene have a Mooney viscosity of at least 10, preferably at least 20, more preferably at least 25, and most preferably at least 30, but not more than 55, preferably not more than 50, and most preferably not more than 45.

In the practice of the invention, it is recommended that the second polybutadiene be one that has been synthesized using a Group VIII catalyst. Exemplary Group VIII catalysts include nickel catalysts and cobalt catalysts.

Examples of suitable nickel catalysts include single-component systems such as nickel-kieselguhr, binary systems such as Raney nickel/titanium tetrachloride, and ternary systems such as nickel compound/organometallic compound/boron trifluoride etherate. Exemplary nickel compounds include reduced nickel on a carrier, Raney nickel, nickel oxide, nickel carboxylate and organonickel complexes. Exemplary organometallic compounds include trialkylaluminum compounds such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum and tri-n-hexylaluminum; alkylolithium compounds such as n-butyllithium, sec-butyllithium, tert-butyllithium and 1,4-dilithiobutane; and dialkylzinc compounds such as diethylzinc and dibutylzinc.

Examples of suitable cobalt catalysts include the following composed of cobalt or cobalt compounds: Raney cobalt, cobalt chloride, cobalt bromide, cobalt iodide, cobalt oxide, cobalt sulfate, cobalt carbonate, cobalt phosphate, cobalt phthalate, cobalt carbonyl, cobalt acetylacetonate, cobalt diethyldithiocarbamate, cobalt anilinium nitrite and cobalt dinitrosyl chloride. It is particularly advantageous to use the above in combination with a dialkylaluminum monochloride such as diethylaluminum monochloride or diisobutylaluminum monochloride; a trialkylaluminum such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum or tri-n-hexylaluminum; an alkyl aluminum sesquichloride such as ethylaluminum sesquichloride; or aluminum chloride.

Polymerization using the Group VIII catalysts described above, and especially a nickel or cobalt catalyst, can generally be carried out by a process in which the catalyst is continuously charged into the reactor together with the solvent and butadiene monomer, and the reaction conditions are suitably selected from a temperature range of 5 to 60° C. and a pressure range of atmospheric pressure to 70 plus atmospheres, so as to yield a product having the above-indicated Mooney viscosity.

It is also desirable for the second polybutadiene in component (b) to satisfy the relationship:

$$20A-750 \leq \eta \leq 20A-550$$

wherein η is the viscosity of the second polybutadiene at 25° C. as a 5 wt % solution in toluene and A is the Mooney viscosity (ML₁₊₄ (100° C.)) of the second polybutadiene.

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The viscosity η is preferably at least 20A-700, more preferably at least 20A-680, and most preferably at least 20A-650, but preferably not more than 20A-560, more preferably not more than 20A-580, and most preferably not more than 20A-590. The use of a polybutadiene having such an optimized relationship of η and A, that suggests the high linearity of polybutadiene molecules, is effective for conferring better resilience and workability.

The second polybutadiene generally accounts for at least 30 wt %, preferably at least 50 wt %, and most preferably at least 70 wt %, and up to 100 wt %, preferably up to 90 wt %, and most preferably up to 80 wt %, of the diene rubber (b). By including the second polybutadiene within component (b) in the foregoing range, even better extrudability and hence, workability during manufacture can be conferred.

The solid core in the golf balls of the invention is molded from a rubber composition containing as essential components specific amounts of (c) an unsaturated carboxylic acid and/or metal salt thereof, (d) an organosulfur compound, (e) an inorganic filler and (f) an organic peroxide per 100 parts by weight of the base rubber.

Specific examples of unsaturated carboxylic acids that may be used as component (c) include acrylic acid, methacrylic acid, maleic acid and fumaric acid. Acrylic acid and methacrylic acid are especially preferred.

Specific examples of unsaturated carboxylic acid metal salts that may be used as component (c) include the zinc and magnesium salts of unsaturated fatty acids such as zinc methacrylate and zinc acrylate. Zinc acrylate is especially preferred.

The unsaturated carboxylic acid and/or metal salt thereof used as component (c) is included in an amount, per 100 parts by weight of the base rubber, of at least 10 parts by weight, preferably at least 15 parts by weight, and most preferably at least 20 parts by weight, but not more than 60 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much component (c) results in excessive hardness, giving the golf ball a feel upon impact that is difficult for the player to endure. On the other hand, too little component (c) undesirably lowers the resilience.

The organosulfur compound (d) of the rubber composition is essential for imparting good resilience. Exemplary organosulfur compounds include thiophenol, thionaphthol, halogenated thiophenols, and metal salts thereof. Specific examples include pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol, and zinc salts thereof, such as the zinc salt of pentachlorothiophenol; and organosulfur compounds having 2 to 4 sulfurs, such as diphenylpolysulfides, dibenzylpolysulfides, dibenzoylpolysulfides, dibenzothiazoylpolysulfides and dithiobenzoylpolysulfides. Diphenyl disulfide and the zinc salt of pentachlorothiophenol are especially preferred.

The organosulfur compound (d) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.2 part by weight, and most preferably at least 0.5 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much organosulfur compound results in an excessively low hardness, whereas too little makes it impossible to enhance the resilience.

Examples of inorganic fillers that may be used as component (e) include zinc oxide, barium sulfate and calcium

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carbonate. The inorganic filler (e) is included in an amount, per 100 parts by weight of the base rubber, of at least 5 parts by weight, preferably at least 7 parts by weight, more preferably at least 10 parts by weight, and most preferably at least 13 parts by weight, but not more than 80 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much or too little inorganic filler makes it impossible to achieve a golf ball core having an appropriate weight and good rebound characteristics.

The organic peroxide (f) may be a commercial product, suitable examples of which include Percumil D (manufactured by NOF Corporation), Perhexa 3M (manufactured by NOF Corporation) and Lupercol 231XL (manufactured by Atochem Co.). If necessary, two or more different organic peroxides may be mixed and used together.

The organic peroxide (f) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.3 part by weight, more preferably at least 0.5 part by weight, and most preferably at least 0.7 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much or too little organic peroxide makes it impossible to achieve a ball having a good feel upon impact and good durability and rebound characteristics.

If necessary, the rubber composition may also include an antioxidant, suitable examples of which include such commercial products as Nocrac NS-6, Nocrac NS-30 (both made by Ouchi Shinko Chemical Industry Co., Ltd.), and Yoshinox 425 (made by Yoshitomi Pharmaceutical Industries, Ltd.). The use of such an antioxidant in an amount, per 100 parts by weight of the base rubber, of at least 0 part by weight, preferably at least 0.05 part by weight, more preferably at least 0.1 part by weight, and most preferably at least 0.2 part by weight, but not more than 3 parts by weight, preferably not more than 2 parts by weight, more preferably not more than 1 part by weight, and most preferably not more than 0.5 part by weight, is desirable for achieving good rebound characteristics and durability.

The solid core of the invention can be produced by vulcanizing and curing the above-described rubber composition using a method like that employed with known rubber compositions for golf balls. For example, vulcanization may be carried out at a temperature of 100 to 200° C. for a period of 10 to 40 minutes.

In the practice of the invention, the solid core has a hardness which is suitably adjusted according to its manner of use in the various golf ball constructions that may be employed and is not subject to any particular limitation. The core may have a cross-sectional hardness profile which is flat from the center to the surface thereof, or which varies from the center to the surface.

It is recommended that the solid core have a deflection, when subjected to a load of 980 N (100 kg), of at least 2.0 mm, preferably at least 2.5 mm, more preferably at least 2.8 mm, and most preferably at least 3.2 mm, but not more than 6.0 mm, preferably not more than 5.5 mm, more preferably not more than 5.0 mm, and most preferably not more than 4.5 mm. Too small a deformation may worsen the feel of the ball upon impact and, particularly on long shots such as with a driver in which the ball incurs a large deformation, may subject the ball to an excessive rise in spin, reducing the carry. On the other hand, if the solid core is too soft, the golf ball tends to have a dead feel when hit, an inadequate

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rebound that results in a poor carry, and a poor durability to cracking with repeated impact.

It is recommended that the solid core in the inventive golf ball have a diameter of at least 30.0 mm, preferably at least 32.0 mm, more preferably at least 34.0 mm, and most preferably at least 35.0 mm, but not more than 40.0 mm, preferably not more than 39.5 mm, and most preferably not more than 39.0 mm.

It is also recommended that the solid core have a specific gravity of at least 0.9, preferably at least 1.0, and most preferably at least 1.1, but not more than 1.4, preferably not more than 1.3, and most preferably not more than 1.2.

The golf ball of the invention is a multi-piece solid golf ball having a cover composed of at least two layers which are referred to herein as the "inner cover layer" and the "outer cover layer." Such cover layers can be produced from known cover stock. The cover stocks used to make both cover layers in the inventive golf ball may be composed primarily of a thermoplastic or thermoset polyurethane elastomer, polyester elastomer, ionomer resin, ionomer resin having a relatively high degree of neutralization, polyolefin elastomer or mixture thereof. Any one or mixture of two or more thereof may be used, although the use of a thermoplastic polyurethane elastomer, ionomer resin or ionomer resin having a relatively high degree of neutralization is especially preferred.

Illustrative examples of thermoplastic polyurethane elastomers that may be used for the above purpose include commercial products in which the diisocyanate is an aliphatic or aromatic compound, such as Pandex T7298, Pandex T7295, Pandex T7890, Pandex TR3080, Pandex T8290, Pandex T8295 and Pandex T1188 (all manufactured by DIC Bayer Polymer, Ltd.). Illustrative examples of suitable commercial ionomer resins include Surlyn 6320, Surlyn 8945, Surlyn 9945 and Surlyn 8120 (both products of E. I. du Pont de Nemours and Co., Inc.), and Himilan 1706, Himilan 1605, Himilan 1855, Himilan 1557, Himilan 1601 and Himilan AM7316 (all products of DuPont-Mitsui Polychemicals Co., Ltd.).

Together with the primary material described above, the cover stock may include also, as an optional material, polymers (e.g., thermoplastic elastomers) other than the foregoing. Specific examples of polymers that may be included as optional constituents include polyamide elastomers, styrene block elastomers, hydrogenated polybutadienes and ethylene-vinyl acetate (EVA) copolymers.

The multi-piece solid golf ball of the invention can be manufactured by any suitable known method without particular limitation. In one preferred method, the solid core is placed within a given injection mold, following which a predetermined method is used to successively inject over the core the above-described inner and outer cover layer materials. In another preferred method, each of the cover stocks is formed into a pair of half cups, and the resulting pairs are successively placed over the solid core and compression molded.

In the golf balls of the invention, it is critical that the outer cover layer have a lower Shore D hardness than the inner cover layer.

It is recommended that the inner cover layer have a Shore D hardness of at least 50, preferably at least 51, more preferably at least 52, and most preferably at least 53, but not more than 80, preferably not more than 75, more preferably not more than 70, and most preferably not more than 65.

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It is recommended that the outer cover layer have a Shore D hardness of at least 35, preferably at least 40, more preferably at least 45, and most preferably at least 48, but not more than 60, preferably not more than 58, more preferably not more than 56, and most preferably not more than 54.

As noted above, in the practice of the invention the outer cover layer must have a lower Shore D hardness than the inner cover layer. It is advantageous for the inner and outer cover layers to have a difference in Shore D hardness of at least 2, preferably at least 5, more preferably at least 7, and most preferably at least 9 Shore D hardness units, but not more than 30, preferably not more than 25, and most preferably not more than 20 Shore D hardness units.

It is recommended that the inner and outer cover layers have a respective thickness of at least 0.7 mm, and preferably at least 1.0 mm, but not more than 3.0 mm, preferably not more than 2.5 mm, even more preferably not more than 2.0 mm, and most preferably not more than 1.6 mm.

The multi-piece solid golf ball of the invention can be manufactured for competitive use by imparting the ball with a diameter and weight which conform with the Rules of Golf; that is, a diameter of at least 42.67 mm and a weight of not more than 45.93 g. It is recommended that the diameter be no more than 44.0 mm, preferably no more than 43.5 mm, and most preferably no more than 43.0 mm; and that the weight be at least 44.5 g, preferably at least 45.0 g, more preferably at least 45.1 g, and most preferably at least 45.2 g.

Multi-piece solid golf balls according to the present invention have a good, soft feel upon impact and an excellent spin performance that enable the ball to travel a greater distance when played.

EXAMPLES

The following examples and comparative examples are provided to illustrate the invention, and are not intended to limit the scope thereof.

Examples 1-5 & Comparative Examples 1-4

The core materials shown in Table 2 were formulated in the indicated amounts per 100 parts by weight of polybutadiene material composed of polybutadiene types (1) to (7) below in the proportions shown in Table 1. The resulting core formulations were blended in a kneader or on a roll mill, then molded under applied pressure at 150° C. for 20 minutes to form solid cores having a diameter of about 36.4 mm.

Types of Polybutadiene

- (1) BR01, made by JSR Corporation
- (2) BR11, made by JSR Corporation
- (3) UBE101, made by Ube Industries, Ltd.
- (4) HCBN-4, an experimental grade of polybutadiene made by JSR Corporation
- (5) HCBN-2, an experimental grade of polybutadiene made by JSR Corporation
- (6) Experimental grade #9100081 made by Firestone
- (7) Experimental grade #9100069 made by Firestone

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TABLE 1

Type	Catalyst	cis-1,4 content, %	1,2 vinyl content, %	Mooney viscosity (A)	Mw/Mn (B)	η	10B + 5	10B + 60	20A - 550
<u>Polybutadiene</u>									
(1)	Ni	96	2.5	44	4.2	150	47	102	330
(2)	Ni	96	2	44	4.4	270	49	104	330
(3)	Co	95	3	38	4.2	130	47	102	210
(4)	Nd	96	1.1	44	3.5	390	40	95	330
(5)	Nd	96	0.9	40	3.3	280	38	93	250
(6)	Nd	95	1.5	56	2.6	370	31	86	570
(7)	Nd	96	1.3	48	2.5	280	30	85	410

TABLE 2

	Example					Comparative Example			
	1	2	3	4	5	1	2	3	4
<u>Rubber formulation (pbw)</u>									
(1)					50				
(2)	70	30	50		50		50		
(3)				50			50		50
(4)	30								
(5)				50	50		50	50	50
(6)		70							
(7)			50						
<u>Core formulation (pbw)</u>									
Polybutadiene	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	1.4	1.4	1.4		0.7	1.4	1.4	1.4	1.4
1,1-Bis(t-butylperoxy)-				0.3	0.3				
3,3,5-trimethylcyclo									
hexane									
Zinc oxide	18	18	15.5	27	26	26	28.5	27	26
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Zinc acrylate	27	27	31	30	32	32	28	30	32
Zinc salt of	1	1	2	1	1	1	0	1	1
pentachlorothiophenol									

The resulting solid cores were tested as described below to determine their deformation under 980 N (100 kg) loading and their rebound. The results are shown in Table 4.

Deformation Under 980 N Loading

Measured as the deflection (mm) of the solid core when subjected to a load of 980 N (100 kg).

Rebound

The initial velocity of the solid cores was measured with the same type of initial velocity instrument as used by the official regulating body—the United States Golf Association (USGA). Each rebound value shown in Table 4 is the difference between the initial velocity of the solid core obtained in that particular example and the initial velocity of the solid core obtained in Comparative Example 2.

In each example, the resulting solid core was placed in a given mold and the appropriate resin shown in Table 3 was injection-molded over the core, thereby producing an inner layer-covered core having a diameter of about 39.7 mm. The covered core was then transferred to a given mold, and the appropriate resin shown in Table 3 was injection molded over the covered core, yielding a three-piece solid golf ball having a diameter of about 42.7 mm and a weight of about 45.3 g. Trade names appearing in Table 3 are described below.

Himilan: An ionomer resin produced by DuPont-Mitsui Polychemicals Co., Ltd.

Surlyn: An ionomer resin produced by E. I. du Pont de Nemours and Co.

Dynaron: An E-EB-E block copolymer produced by JSR Corporation.

Pandex: A polyurethane elastomer produced by Bayer-DIC Polymer, Ltd.

The properties of the resulting golf balls were determined as described below. The results are shown in Table 4.

Material Properties

The Shore D hardnesses of the inner cover layer and the outer cover layer were measured with a durometer by the test method described in ASTM D2240.

Golf Ball Properties

The carry and total distance were measured when the ball was hit at a head speed (HS) of 50 m/s with a driver (No. 1 Wood) mounted on a swing machine.

Feel

The feel of the ball when actually shot with a driver (No. 1 Wood) and putter was rated by five professional and five top-caliber amateur golfers as "Too hard," "Good" or "Too soft." The rating assigned most often to a particular ball was used as that ball's overall rating.

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TABLE 3

	A	B	C	D	E	F	G
Formulation (pbw)							
Himilan 1706	50	70					
Himilan 1605	50						
Himilan 1557						20	
Himilan 1855						30	
Himilan AM7316		12					
Surlin 8945			35				
Surlin 9945			35				
Surlin 8120				100		50	
Dynarcon 6100P			30				
Pandex T8290					50		15
Pandex T8295					50	100	
Behenic acid		16					
Magnesium oxide		2					
Titanium dioxide	4	2	4	4	2.7	2.7	4 20

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Japanese patent application Ser. No. 2001-163238 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

What is claimed is:

1. A multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, wherein the solid core is molded from a rubber composition comprising

100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity η at 25° C. as a 5 wt % solution in toluene of up to 600 mPa s, being synthesized using a rare-earth catalyst and satisfying the relationship: $10B + 5 \leq A \leq 10B + 60$, wherein A is the Mooney viscosity (ML_{1+4} (100° C)) of the polybutadiene and B is the ratio M_w/M_n between the weight-average molecular weight M_w and the number-average molecular weight M_n of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a),

TABLE 4

	Example					Comparative Example				
	1	2	3	4	5	1	2	3	4	
<u>Core properties</u>										
Deflection (mm) under 980 N load	3.8	3.8	3.5	3.5	3.5	3.3	3.5	3.5	3.3	
Specific gravity	1.15	1.15	1.15	1.21	1.21	1.21	1.21	1.21	1.21	
Rebound (m/s)	+0.9	+0.9	+1.1	+0.7	+0.8	+0.3	0	+0.5	+0.5	
<u>Inner cover layer</u>										
Type	A	B	C	A	B	B	A	D	D	
Shore D hardness	63	60	56	63	60	60	63	45	45	
Specific gravity	0.98	0.97	0.97	0.98	0.97	0.97	0.98	0.98	0.98	
Thickness (mm)	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	
<u>Outer cover layer</u>										
Type	E	F	F	G	G	G	G	G	A	
Shore D hardness	47	51	51	53	53	53	53	53	63	
Specific gravity	1.18	1.18	1.18	0.98	0.98	0.98	0.98	0.98	0.98	
Thickness (mm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	
<u>Golf ball properties</u>										
When hit with No. 1 Wood at HS of 50 m/s										
Carry (m)	227.0	226.9	226.7	226.9	226.7	223.8	222.2	217.7	220.8	
Total distance (m)	258.5	258.8	258.3	258.3	258.0	255.0	253.4	248.3	252.8	
Spin rate (rpm)	3205	3153	3241	3125	3180	3182	3121	3305	3177	
Feel on impact	good	good	good	good	good	good	good	too soft	good	
Spin rate on approach shot (sand wedge; HS 20 m/s)	6323	6251	6236	6118	6111	6107	6113	6186	4308	
Feel of ball	good	good	good	good	good	good	good	too soft	too hard	

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(c) 10 to 60 parts by weight of an unsaturated carboxylic acid or a metal salt thereof or both,
 (d) 0.1 to 5 parts by weight of an organosulfur compound,
 (e) 5 to 80 parts by weight of an inorganic filler,
 (f) 0.1 to 5 parts by weight of an organic peroxide;
 the inner cover layer has a Shore D hardness of 50 to 80;
 the outer cover layer has a Shore D hardness of 35 to 60;
 and
 the outer cover layer has a lower Shore D hardness than
 the inner cover layer.
 2. The golf ball of claim 1, wherein the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity (ML_{1+4} (100° C.)) of not more than 55, and satisfies the relationship:
 $\eta \leq 20A - 550$,
 wherein A is the Mooney viscosity (ML_{1+4} (100° C.)) of the second polybutadiene and η is the viscosity of the second polybutadiene, in mPa-s, at 25° C. as a 5 wt % solution in toluene.

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3. The golf ball of claim 1 wherein said polybutadiene (a) is synthesized by using neodymium catalyst.
 4. The golf ball of claim 1 wherein said polybutadiene (a) has a Mooney viscosity (ML_{1+4} , 100° C.) of 40 to 60.
 5. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 5 units.
 6. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 7 units.
 7. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 9 units.
 8. The golf ball of claim 1, wherein said ball is three-piece construction consisting of a solid core, an inner cover layer and an outer cover layer.
 9. The golf ball of claim 2, wherein the second polybutadiene in component (b) is synthesized using a Group VIII catalyst.

* * * * *

EXHIBIT I



US005743817A

United States Patent [19] Yamagishi et al.

[11] Patent Number: 5,743,817
[45] Date of Patent: Apr. 28, 1998

[54] GOLF BALL

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4,919,434 4/1990 Saito 473/376
5,304,608 4/1994 Yabaki et al 473/372 X
5,516,110 5/1996 Yabaki et al 473/372

FOREIGN PATENT DOCUMENTS

[73] Assignee: Bridgestone Sports Co., Ltd., Tokyo,
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2276628 10/1994 United Kingdom

[21] Appl. No.: 536,049

[22] Filed: Sep. 29, 1995

[30] Foreign Application Priority Data

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Dec. 14, 1994 [JP] Japan 6-333024

[51] Int. CL⁶ A63B 37/06; A63B 37/12

[52] U.S. CL 473/377; 473/351; 473/385

[58] Field of Search 473/372, 373,
473/351, 377, 385, 370, 374, DIG. 22

[56] References Cited

U.S. PATENT DOCUMENTS

4,858,924 8/1989 Saito et al. 473/373

Primary Examiner—George J. Marlo

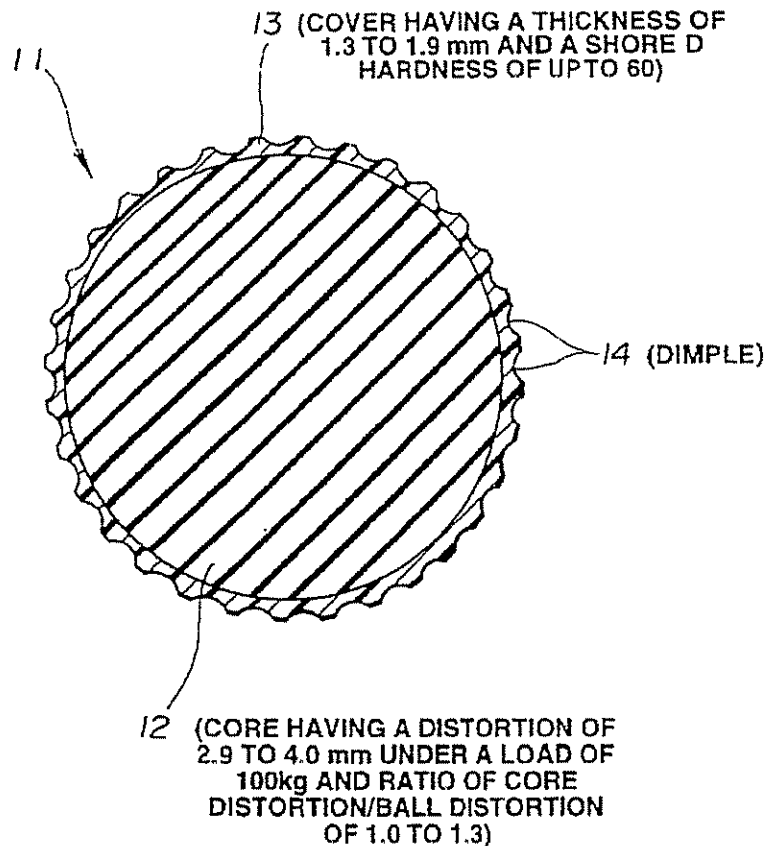
Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak
& Seas, PLLC

[57]

ABSTRACT

A solid golf ball comprising a core and a cover is provided. The core has a core hardness expressed by a distortion of 2.2–4.0 mm under a load of 100 kg. The core hardness divided by the ball hardness ranges from 1.0 to 1.3. The cover has a thickness of 1.3–1.8 mm. The ball is improved in feel and spin while maintaining the flying distance inherent to solid golf balls.

2 Claims, 1 Drawing Sheet

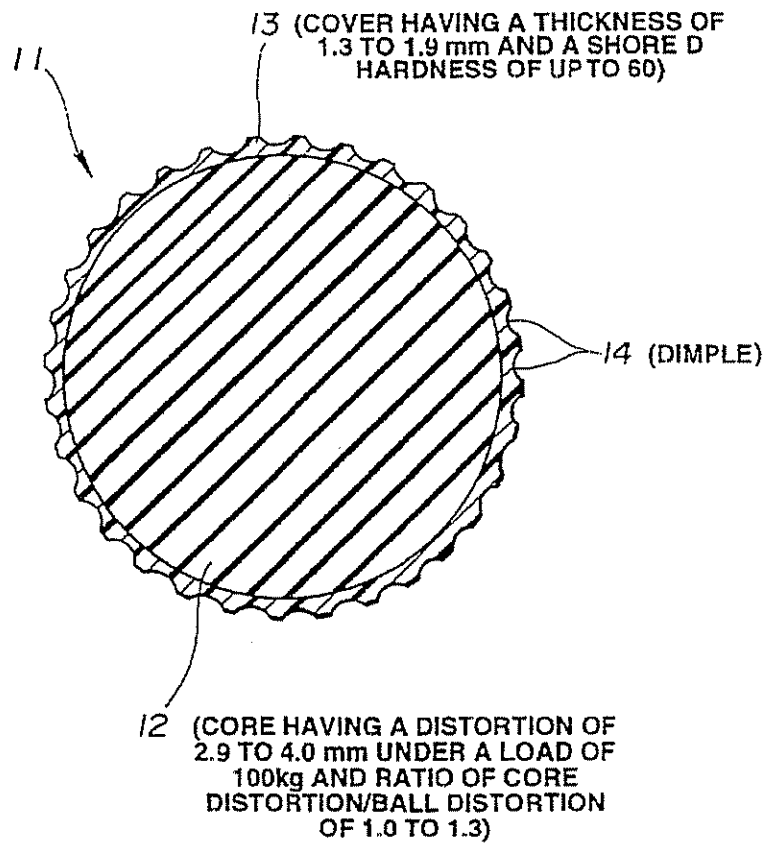


U.S. Patent

Apr. 28, 1998

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FIG. 1



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GOLF BALL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a solid golf ball having improved feel and spin performance.

2. Prior Art

As compared with wound golf balls, two-piece golf balls and other solid golf balls are advantageous in gaining a flying distance since they fly along the trajectory of a straight ball when hit by both drivers and irons. This advantage is mainly attributable to their structure. Because of their configuration less receptive to spin, the solid golf balls are given a straight ball trajectory and yield a more run, resulting in an increased total flying distance.

In turn, the solid golf ball tends to draw a "flier" path on an iron shot since it is less receptive to spin and does not readily stop on the green. Because of such characteristics, the two-piece balls are not preferred by experienced players.

Therefore, there is a need for a solid golf ball having improved spin properties and allowing the player to aim the pin dead with an iron. The increased flying distance inherent to the solid golf ball should be maintained and of course, the ball should have a pleasant feel.

SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a solid golf ball such as a two-piece golf ball which is improved in feel, spin properties and iron control without detracting from the trajectory and flying distance inherent to the solid golf ball. The term iron control is the controllability of a ball on an iron shot, more specifically stop on the green.

Briefly stated, the present invention pertains to a solid, typically two-piece, golf ball comprising a core and a cover enclosing the core. The hardness of the core, cover and ball are referred to as core hardness, cover hardness, and ball hardness, respectively. According to the invention, the core hardness is such that the core undergoes a distortion of at least 2.2 mm under a load of 100 kg. The core hardness divided by the ball hardness is in the range of 1.0 to 1.3. The cover has a radial thickness of 1.3 to 1.8 mm. This parameter control leads to a golf ball satisfying the requirements of flying distance, feel and spin.

Consider the spin mechanism of golf balls made of the same materials, but changed in hardness. Provided that the club head speed and the cover material are identical, the coefficient of friction between the ball and the club face is identical and hence, an identical frictional force is exerted therebetween. Only distortion is different due to differential hardness. Then the distance between the center of gravity and the ball-club contact point is different. The harder the ball, the longer is the contact point distance. The softer the ball, the shorter is the contact point distance. Then harder balls are more receptive to spin.

The spinning mechanism associated with an iron suggests that the spin quantity can be increased by increasing the ball hardness. Increasing the ball hardness, however, gives a harder feel, exacerbating the hitting feel. The spin quantity can also be increased by making the cover softer. A softer cover, however, deprives the ball of repulsion, resulting in a loss of initial speed and flying distance.

Attempting to increase the spin quantity for improving spin properties by using a soft material, typically a material having a Shore D hardness of 60 or lower as the cover, we found that a low hardness cover lowers repulsion, resulting

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in a loss of flying distance on hitting. Quite unexpectedly, we have found that by adjusting the core hardness to a distortion of at least 2.2 mm under a load of 100 kg, the ratio of core hardness to ball hardness to range from 1.0 to 1.3 and the cover thickness to range from 1.3 mm to 1.8 mm, the golf ball, whose cover is made of a softer material, is improved in iron control (that is, stop on the green) without deterring the feel and flying distance and without losing the trajectory and flying distance on a driver shot inherent to solid golf balls.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic cross section illustrating one embodiment of the golf ball of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the golf ball comprising a spherical solid core enclosed in a cover according to the present invention, the core hardness is at least 2.2 mm as expressed by a distortion under a load of 100 kg, the core hardness divided by the ball hardness is in the range of 1.0 to 1.3 and the cover has a thickness of 1.3 to 1.8 mm.

The core hardness and ball hardness are defined by distortions (in mm) of the core and ball under a load of 100 kg, respectively. The core hardness corresponds to such a distortion of at least 2.2 mm, preferably at least 2.5 mm, more preferably 2.5 to 4.0 mm, most preferably 3.0 to 4.0 mm. With a core distortion of less than 2.2 mm, the feel becomes unpleasant. Too much core distortions would result in balls having poor restitution, low flying performance and a too soft feel. By controlling the core hardness/ball hardness so as to fall in the range between 1.0 and 1.3, especially between 1.0 and 1.25, the solid golf ball, typically two-piece golf ball is improved in feel, flying distance and spin characteristics. If the core hardness/ball hardness is less than 1.0, the feel becomes unpleasant. If the core hardness/ball hardness exceeds 1.3, the ball loses a quick stop on the green.

It is understood that the golf ball of the invention is advantageously applied to two-piece golf balls having a single core. It is also applicable to multi-core golf balls having a core consisting of two or more layers, such as three-piece golf balls. In an example where the core consists of two inner and outer layers, the core hardness refers to the hardness of the spherical two-layer core as a whole. Differently stated, the core hardness refers to the hardness of an entire spherical core left after removing the cover from the ball.

The cover has a Shore D hardness of up to 60, especially 55 to 60. A cover hardness of more than 60 would adversely affect spin characteristics and stop on the green. Since a cover with too low hardness would result in poor repulsion and a loss of flying distance, the lower limit of 55 is recommended for the cover hardness.

According to the invention, the cover has a radial thickness of 1.3 to 1.8 mm, especially 1.4 to 1.8 mm. Outside the range, the objects of the invention cannot be achieved. A cover of thinner than 1.3 mm is less resistant against top damage and liable to be broken. A cover of thicker than 1.8 mm leads to losses of repulsion and flying performance and gives a dull feel.

In general, the flying distance the ball covers depends on the head speed. The flying distance is reduced by a change from a higher head speed to a lower head speed. The degree

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of reduction of the flying distance by a change from a higher head speed to a lower head speed can be suppressed by limiting the cover thickness to the above-defined range. Differently stated, the dependency of flying distance on head speed is alleviated. Therefore, the ball of the invention is suitable for senior and female players who swing at a relatively low head speed.

In one preferred embodiment of the invention, the golf ball has a spin factor of 1.0 to 1.5. The spin factor is defined as follows. The golf ball has a spin quantity when hit by a pitching wedge (referred to as wedge spin quantity) and a spin quantity when hit by a driver (referred to as driver spin quantity). The spin factor is obtained by dividing the ratio of the wedge spin quantity to the driver spin quantity by the ball hardness. Then a spin factor smaller than unity means that the ball has greater spin with the driver and less spin with the pitching wedge. The former indicates that the trajectory is lofted and the flying distance is reduced. The latter indicates that when hit with an iron, the ball draws a flatter-like trajectory and flies too much. A greater spin factor is then desirable. Then the object of the invention to render the ball receptive to less spin with a driver and more spin with an iron is effectively accomplished. However, a too greater spin factor would exacerbate ball control on an iron shot because the ball can be moved back too much due to back spin. For this reason, the spin factor is preferably in the range between 1.0 and 1.5.

The golf ball of the invention is advantageously applied to two-piece golf balls while it is also applicable to multi-core golf balls such as three-piece golf balls. The material and preparation of the core and cover are not critical. The components may be made of any of well-known materials insofar as the requirements of the invention are met. Of course, the golf ball of the invention has a standard size and weight.

More particularly, the core of the present solid golf ball is formed from a rubber composition by a conventional method while properly adjusting the component proportion and vulcanizing conditions. The core composition generally includes a base rubber, a crosslinking agent, a co-crosslinking agent, an inert filler, and other components. The base rubber may be selected from natural and synthetic rubbers conventionally used in the manufacture of solid golf balls. Preferably the base rubber is 1,4-polybutadiene rubber containing at least 40% of cis-configuration, optionally in admixture with natural rubber, polyisoprene rubber or styrene-butadiene rubber. The crosslinking agent is preferably selected from organic peroxides such as dicumyl peroxide and di-t-butyl peroxide, with the dicumyl peroxide being more preferred. Preferably the crosslinking agent is blended in an amount of about 0.5 to 3 parts, more preferably about 0.8 to 1.5 parts by weight per 100 parts by weight of the base rubber. Non-limiting examples of the co-crosslinking agent include metal salts of unsaturated fatty acids, especially zinc and magnesium salts of unsaturated fatty acids having 3 to 8 carbon atoms, such as acrylic acid and methacrylic acid. Zinc acrylate is the most preferred salt. The co-crosslinking agent is preferably blended in an amount of about 24 to 38 parts, more preferably about 28 to 34 parts by weight per 100 parts by weight of the base rubber. Examples of the inert filler include zinc oxide, barium sulfate, silica, calcium carbonate, and zinc carbonate, with the zinc oxide being most often used. The amount of the filler blended depends on the desired specific gravity of the core and cover, ball weight, and other factors although it generally ranges from about 10 to about 60 parts by weight per 100 parts by weight of the base rubber.

These components are blended to form a core-forming rubber composition which is kneaded by means of a conventional kneading machine such as a Banbury mixer and

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roll mill and then compression or injection molded in a spherical mold cavity. The molded composition is cured by heating it at a sufficient temperature for the crosslinking and co-crosslinking agents to exert their function (for example, about 130° to 170° C. when the crosslinking agent is dicumyl peroxide and the co-crosslinking agent is zinc acrylate). In this way, a solid spherical core having a diameter of 37 to 40 mm is prepared.

In the case of a two layer core, the inner core may be made of the same composition as above and the outer core may be made of a similar rubber composition or a resin composition based on an ionomer resin or the like. The outer core may be formed by compression molding or injection molding it around the inner core. Typically the inner core has a diameter of 27.0 to 38.0 mm, preferably 28.0 to 36.0 mm and the outer core has a diameter of 0.5 to 6.5 mm, preferably 1.5 to 5.5 mm, and the total diameter ranges from 37 to 40 mm.

The solid core is enclosed with the cover by any desired technique, for example, by enclosing the core in a pair of semi-spherical shell halves followed by heat compression molding. Alternatively the core is directly covered with a cover material by injection molding. By properly selecting the material and amount of the core and cover and preparation conditions such as vulcanizing conditions, a golf ball satisfying the requirements of the invention can be prepared.

There has been described a golf ball which is improved in feel and spin characteristics while maintaining the flying distance inherent to solid golf balls and which undergoes a lower degree of reduction of its flying distance upon hitting at a lower head speed.

EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation.

Examples 1-6 and Comparative Examples 1-2

Cores having a hardness as shown in Table 1 were molded by vulcanizing in a mold rubber compositions comprising cis-1,4-polybutadiene rubber, zinc acrylate, zinc oxide, and dicumyl peroxide. The core hardness reported is a distortion in millimeter under a load of 100 kilograms.

The cores were enclosed with covers which were formed from mixtures of ionomer resins. The blending proportion of ionomer resins was changed to form covers having varying hardness (Shore D scale) as shown in Table 2. In this way, there were obtained large-size two-piece golf balls having a hardness as shown in Table 3. The ball hardness reported is again a distortion in millimeter under a load of 100 kilograms.

The base composition for the core consisted of the following components.

Parts by weight	
cis-1,4-polybutadiene rubber (BRD1)	100
zinc acrylate	33.2
zinc oxide	10
barium sulfate	9.7
anti-oxidant	0.2
dicumyl peroxide	0.9

Cores having varying hardness and specific gravity were obtained by varying the amounts of zinc acrylate and barium sulfate as shown in Table 1.

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TABLE 1

Core hardness	Cover gage				
	1.4 mm	1.6 mm	1.8 mm	2.0 mm	2.4 mm
2.48-2.50 mm	33.0	33.0	33.0	33.0	
	6.4	7.5	8.6	9.7	
2.88-2.91 mm	31.0	31.0	31.0	31.0	31.0
	7.8	8.8	9.9	11.0	13.9
3.25-3.30 mm	28.0	28.0	28.0	28.0	
	9.1	10.2	11.2	12.3	

At the upper and lower stages for each core hardness and cover gage combination, the amounts of zinc acrylate and barium sulfate are reported in parts by weight, respectively.

The base composition for the cover was a 50/50 (by weight) mixture of ionomer resins, Himilan 1650 and Surlyn

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Stop on the Green Test

Using a swing robot manufactured by True Temper Co., the ball was hit by a pitching wedge at a head speed of 35 m/s so as to fly directly on the green. The distance between the landing and stop positions was measured. A negative value is the distance the ball covers due to back spin. A positive value is a run in a flying direction. The stop on the green was rated "O" for quick stop and "X" for non-stopping.

Feel Test

In a sensory test, a player hit the ball at a head speed (HS) of 35 m/s. The ball feel was rated "very soft", "soft" or "hard".

Note that the dependency of flying distance on head speed is expressed by the flying distance at a head speed of 35 m/s divided by the flying distance at a head speed of 45 m/s and simply reported under the heading "HS35/HS45" in Table 3.

TABLE 3

	Example						Comparative Example	
	1	2	3	4	5	6	1	2
Core hardness (mm)	2.48	3.30	2.50	2.90	2.91	3.25	2.10	2.85
Ball hardness (mm)	2.36	3.10	2.30	2.71	2.65	2.90	1.90	2.10
Core/ball hardness ratio	1.05	1.06	1.09	1.07	1.10	1.12	1.11	1.36
Cover thickness (mm)	1.4	1.4	1.6	1.6	1.8	1.8	1.8	2.4
Cover hardness (Shore D)	56	57	56	56	56	57	57	65
Feel @ HS35	soft	very soft	soft	very soft	soft	very soft	hard	soft
Flying distance (m)								
@ HS 35	154	160	154	158	157	159	147	148
@ HS 45	234	237	232	233	233	236	228	235
Stop on the green								
Landing-to-stop distance (m)	-0.5	0.5	0.0	0.0	0.0	-0.5	0.0	2.5
Rating	o	o	o	o	o	o	o	x
HS35/HS45	0.658	0.675	0.664	0.678	0.674	0.673	0.645	0.630

8120. Covers having varying hardness were obtained while blending Himilan 1650 and Surlyn 8120 in a ratio as shown in Table 2

TABLE 2

Cover hardness (Shore D)	Resin mix	Weight ratio
56	H1650/S8120	40/60
57	H1650/S8120	50/50
65	H1605/H1706	50/50

* H: Himilan commercially available from du Pont-Mitsui Polychemical Co. Ltd.

S: Surlyn commercially available from E. I. duPont

The golf balls were examined for fly, stop on the green, and feel by the following procedures.

Fly Test

Using a swing robot manufactured by True Temper Co., the ball was hit by a driver at a head speed (HS) of 45 m/s and by an iron at a head speed of 35 m/s to measure the flying distance.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. A golf ball comprising a core and a cover wherein said core and said ball has a core hardness and a ball hardness respectively, wherein said core has a distortion of 2.9 to 4.0 mm under a load of 100 kg, the ratio of a core distortion under a load of 100 kg divided by a ball distortion under a load of 100 kg ranges from 1.0 to 1.3, and said cover consists of an ionomer resin as a resin component and has a thickness of 1.3 to 1.8 mm and a Shore D hardness of up to 60.

2. The golf ball of claim 1 wherein said cover has a thickness of 1.6 to 1.8 mm.

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